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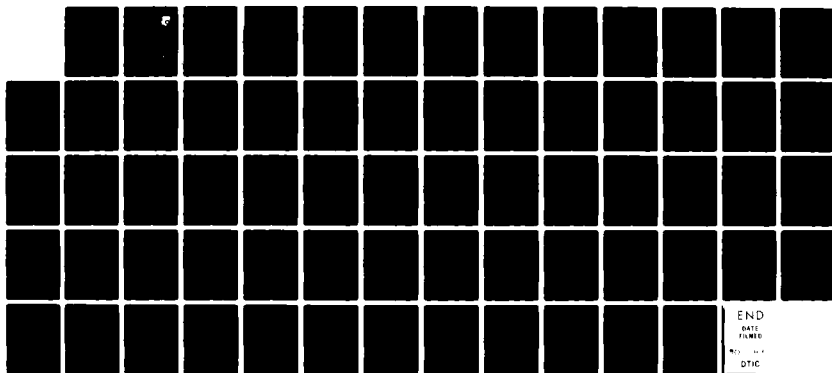
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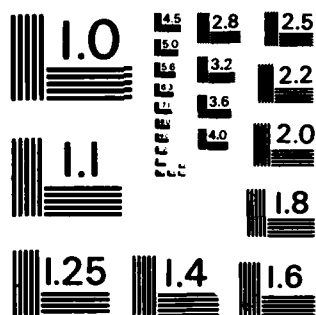
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CALCIUM-THIONYL CHLORIDE BATTERY TECHNOLOGY



T. Potts

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JUNE 1983

INTERIM REPORT FOR PERIOD MARCH 1982 - MAY 1983

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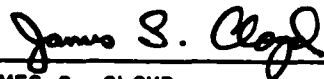
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This technical report has been reviewed and is approved for publication.



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The purpose of this program segment is to improve the calcium-thionyl chloride technology in order to produce a power cell with an acceptable shelf life. This task involves efforts to further develop a basic understanding of the electrochemical behavior of the cell components. Component stability tests, quality control techniques, cathode optimization studies, and electrochemical research all aid in the determination of the calcium corrosion reaction mechanism. Knowledge of the corrosion mechanism is a necessary step toward passivating the calcium anode or removing the		

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### SUMMARY

The kinetics and mechanism of the anodic dissolution of calcium in  $\text{LiAlCl}_4/\text{SOCl}_2$  and  $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$  electrolytes were determined using rapid scan chronopotentiometric and galvanostatic polarization techniques. Preliminary results reveal that while the one-charge-transfer reaction via rapid scan chronopotentiometric polarization involves the adsorption of  $\text{AlCl}_4^-$  on the metal surface for both electrolytes, the steady-state, two-charge-transfer reaction via galvanostatic polarization shows a distinctly different mechanism for each electrolyte. In  $\text{LiAlCl}_4$  electrolyte, a pure charge transfer reaction is observed and the reaction rate is independent of the electrolyte concentration. In  $\text{Ca}(\text{AlCl}_4)_2$  electrolyte, however, the charge transfer reaction is accompanied by  $\text{AlCl}_4^-$  adsorption and the rate of anodic dissolution depends on the electrolyte concentration.

Calcium metal in thionyl chloride shows no corrosion after 23 weeks at  $+55^\circ\text{C}$ . Thionyl chloride containing sulfur or  $\text{HCl}$  produces no calcium corrosion after 23 weeks at  $+55^\circ\text{C}$ . Thionyl chloride containing  $\text{LiAlCl}_4$  or  $\text{Ca}(\text{AlCl}_4)_2$  causes calcium metal to corrode after six weeks at  $+55^\circ\text{C}$ . Alloying calcium with aluminum, copper, lithium, or mercury does not improve its storage characteristics in thionyl chloride electrolyte containing aluminum. The presence of hydrolysis products ( $\text{OH}^-$ ) in thionyl chloride electrolyte containing aluminum reduces the storage time. Various degrees of calcium purity, the least being 99%, produces no effect on calcium storage.

Electrolytes containing aluminum are likely to dissolve or react with the binder in glass separator material. The separator used with thionyl chloride electrolytes should be a pressed or woven glass which does not contain a binder material. Both the Manning Paper Company and the C.H. Dexter Company produce such separator material (both separators have excellent mechanical properties). While yttria oxide separator appears compatible with thionyl chloride electrolyte, the separator is poorly bound together thus giving it poor mechanical and handling properties.

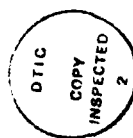
Calcium metal resists corrosion in oxyhalide solvents containing no electrolyte salts. However, corrosion occurs in the presence of electrolyte containing  $\text{LiAlCl}_4$  or  $\text{Ca}(\text{AlCl}_4)_2$ . Calcium corrosion in  $\text{Ca}(\text{AlCl}_4)_2$  electrolyte occurs faster than the corrosion in  $\text{LiAlCl}_4$  electrolyte. Storage tests show that corrosion in  $\text{LiAlCl}_4$  electrolyte is not reduced with decreases in the  $\text{LiAlCl}_4$  concentration. The calcium surface condition such as a polished metallic surface or calcium oxide film does not improve compatibility in  $\text{LiAlCl}_4$  electrolyte. Also, the use of a vinyl polymer additive does not improve the storability of calcium in aluminum-containing electrolyte.

Cathodes have been fabricated which produce  $0.50 \text{ AH/cm}^3$ . This represents a 40% improvement over cathodes produced in earlier efforts. The improved cathodes contain 95% carbon black with 5% Teflon binder and are formed by pressing dry cathode material to form the cathode. The resulting cathode is dried at  $+100^\circ\text{C}$ . Maximum cathode performance is achieved when the cathodes are discharged from 1.0 to  $1.4 \text{ mA/cm}^2$ .

# PREFACE

This Interim Report documents the efforts conducted by Eagle-Picher Industries, Inc. in compliance with Contract F33615-81-C-2076. Submission of this report is to the Air Force Wright Aeronautical Laboratories; Wright-Patterson Air Force Base, Ohio. The object of this task was to study and improve the storage of calcium anodes in thionyl-chloride electrolyte.

Eagle-Picher Industries thanks J. S. Cloyd of the Wright Aeronautical Laboratories for his assistance in this portion of the program.



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## SECTION I

### INTRODUCTION

Earlier research into the calcium/thionyl chloride system has shown the system to possess improved safety characteristics and stability under abusive conditions when compared to the lithium/thionyl chloride couple. Earlier studies have also shown that the calcium/thionyl chloride system needs additional development in the areas of storage performance and rate capabilities.

The purpose of this effort is to advance the calcium/thionyl chloride technology in order to produce an optimized cell suitable for aircrew life support equipment. The total effort consists of two tasks. The first task is to develop a basic understanding of chemical and electrochemical behavior of cell components, quality control, and cell operation. Goals in the first task will be achieved through component stability and storability studies, quality control techniques, and cathode optimization studies. Task II efforts involve demonstrating an optimized cell design resulting from the efforts initiated in Task I.

## SECTION II

### COMPONENT STORAGE PERFORMANCE

Two simultaneous efforts were undertaken in order to determine the factors which cause calcium anodes to corrode in thionyl chloride electrolyte. One approach was to use electrochemical investigation techniques to provide the knowledge of the kinetics and mechanism of the anodic dissolution of calcium in the electrolyte solution. The second approach was the removal of any contaminating species in the cell components which may cause calcium corrosion. This approach

included the purification of cell materials followed by compatibility tests of the purified materials. Purification of cell materials and/or the use of alternate materials assisted in determining the mechanism of the calcium corrosion.

#### Anode Development

Anode material containing 99% calcium, .7% magnesium, and .3% aluminum, was obtained from Pfizer, Inc., Wallingford, Ct. This material was rolled to .040 inches. The annealing process involved heating the calcium to 850°F under an argon atmosphere of .007 mm Hg. The purity on a metals basis was determined by atomic absorption. Storage of the calcium was under mineral oil. An improved purity of calcium was supplied by Alfa Products, Danvers, Mass. This material was 99.8% calcium. The material was in the form of turnings which were not annealed. Pfizer later produced another calcium foil containing 99.9% calcium on a metals basis. The major metal contaminant was magnesium at .027%. This foil was also annealed and stored under mineral oil.

Alfa Products supplied three calcium alloys. The Ca: Cu, Ca: Al, and Ca: Li contained 90% calcium. The materials were in ingot form and were not annealed. Another alloy, Ca: Hg, was produced in a glovebox at less than 10 ppm H<sub>2</sub>O using Pfizer 99.97% calcium. The calcium amalgam was produced on the surface of the calcium by immersing the calcium in mercury. The calcium alloys' resistance to corrosion was evaluated through compatibility storage tests.

### Electrolyte Materials

Thionyl chloride for use in the calcium storage tests was obtained from three sources: Lithcoa, Apache, and Eagle Picher. Lithcoa supplied 1.5M  $\text{LiAlCl}_4$  electrolyte. Manufacturers' stated concentration was confirmed by atomic absorption detection of the metals present. Iron content was never more than 5 ppm. The color of the Lithcoa material was pale yellow. Apache supplied 1.4M  $\text{LiAlCl}_4$  electrolyte which was dark blue or black in color.

Hydrolysis products and HCl contaminants were determined using an Acculab II I.R. Spectrophotometer. Quartz I.R. cells were dried before filling within a glove box containing less than 10 ppm  $\text{H}_2\text{O}$ . Spectrographs showing reduced transmission at the  $3310\text{ cm}^{-1}$  band indicates the presence of hydrolysis products. Reduced transmission at the  $2770\text{ cm}^{-1}$  band indicates the presence of HCl. From sample to sample, changes in contaminant concentrations were detected by the changes in the % of transmission.

Figure 1 is a spectrograph of Lithco 1.5M  $\text{LiAlCl}_4$  in thionyl chloride. Reduced transmission at  $3310\text{ cm}^{-1}$  indicates hydrolysis products contamination. Also indicated is the presence of HCl at  $2770\text{ cm}^{-1}$ .

Figure 2 is a spectrograph of Apache 1.4M  $\text{LiAlCl}_4$  in thionyl chloride. Reduced transmission at  $3310\text{ cm}^{-1}$  indicates hydrolysis products contamination. HCl presence is confirmed at  $2770\text{ cm}^{-1}$ . Comparing Figures 1 and 2 indicates that Lithcoa contains approximately the same amount of HCl contamination.

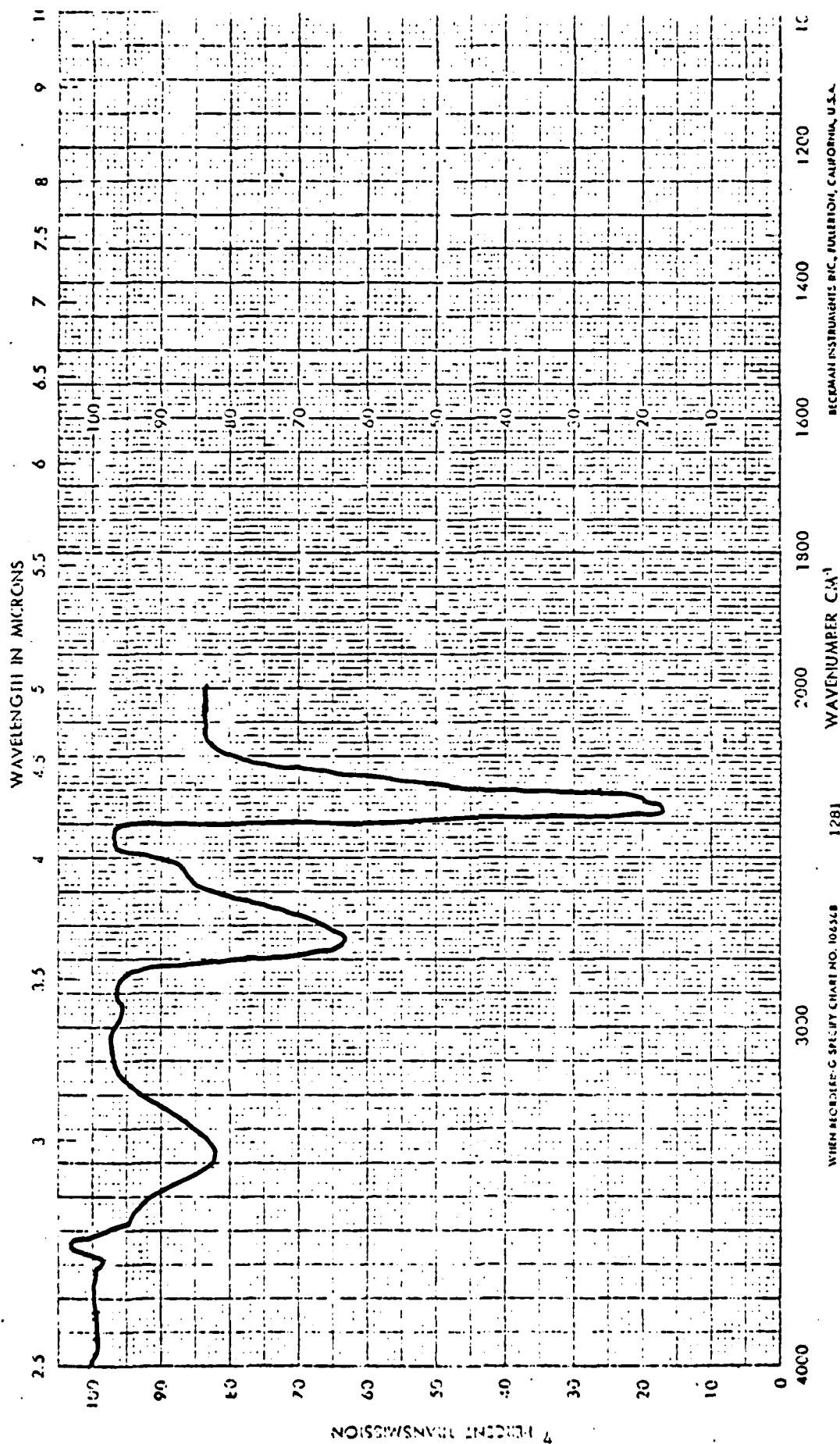


Figure 1. Lithcoa 1.5H LiAlCl<sub>4</sub>

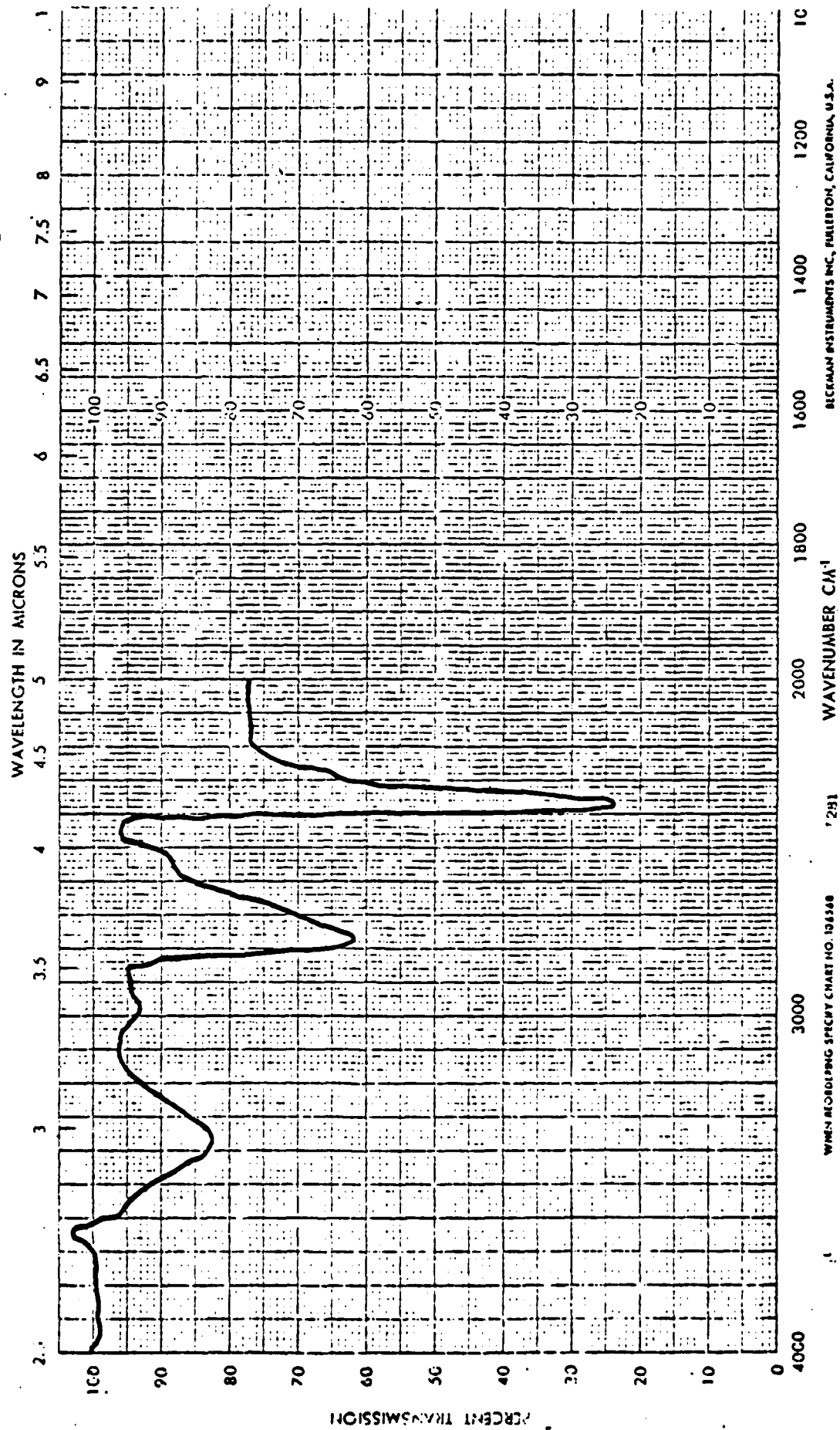


Figure 2. A<sub>2</sub>Ac<sub>2</sub> 1.4M LiAlCl<sub>4</sub>



Other 1.5M  $\text{LiAlCl}_4$  electrolyte was produced by reacting  $\text{AlCl}_3$  and  $\text{LiCl}$  in thionyl chloride at room temperature. Thionyl chloride was obtained from Eastman Kodak and Fluka. Figure 3 is a spectrograph of the Eastman Kodak material. The reduced transmission at  $2770\text{ cm}^{-1}$  indicates the presence of  $\text{HCl}$ . Figure 4 is a spectrograph of the Fluka material. Unknown contamination in the Fluka material resulted in reduced transmission at  $3230\text{ cm}^{-1}$ . The  $\text{HCl}$  content in the Fluka material resulted in reduced transmission at  $3230\text{ cm}^{-1}$ . The  $\text{HCl}$  content in the Fluka material appears to be greater than the  $\text{HCl}$  content in the Eastman Kodak material, Figure 3. The Eastman Kodak thionyl was chosen as the solvent in electrolyte preparation. Distillation, refluxing, and stripping failed to improve the purity of the Eastman Kodak material. The  $\text{AlCl}_3$  and  $\text{LiCl}$  salts were supplied by Fluka.

The first lot of 1.5M ( $\text{LiAlCl}_4$ ) electrolyte was prepared in a glove box containing less than 10 ppm  $\text{H}_2\text{O}$ . All materials were used as received from the suppliers. Aluminum chloride was first dissolved in thionyl chloride. An excess amount of  $\text{LiCl}$  was then added to form  $\text{LiAlCl}_4$ . The resulting electrolyte produced the spectrograph in Figure 5. Large amounts of hydrolysis products and  $\text{HCl}$  are indicated.

A second lot of (1.5M  $\text{LiAlCl}_4$ ) electrolyte was prepared using purified salts. The Fluka  $\text{AlCl}_3$  was sublimed at  $+124^\circ\text{C}$  and 1 mmHg. The Fluka  $\text{LiCl}$  was dried at  $+160^\circ\text{C}$  and 1 mmHg for 16 hours. The mixing technique was identical to that of the first lot. The

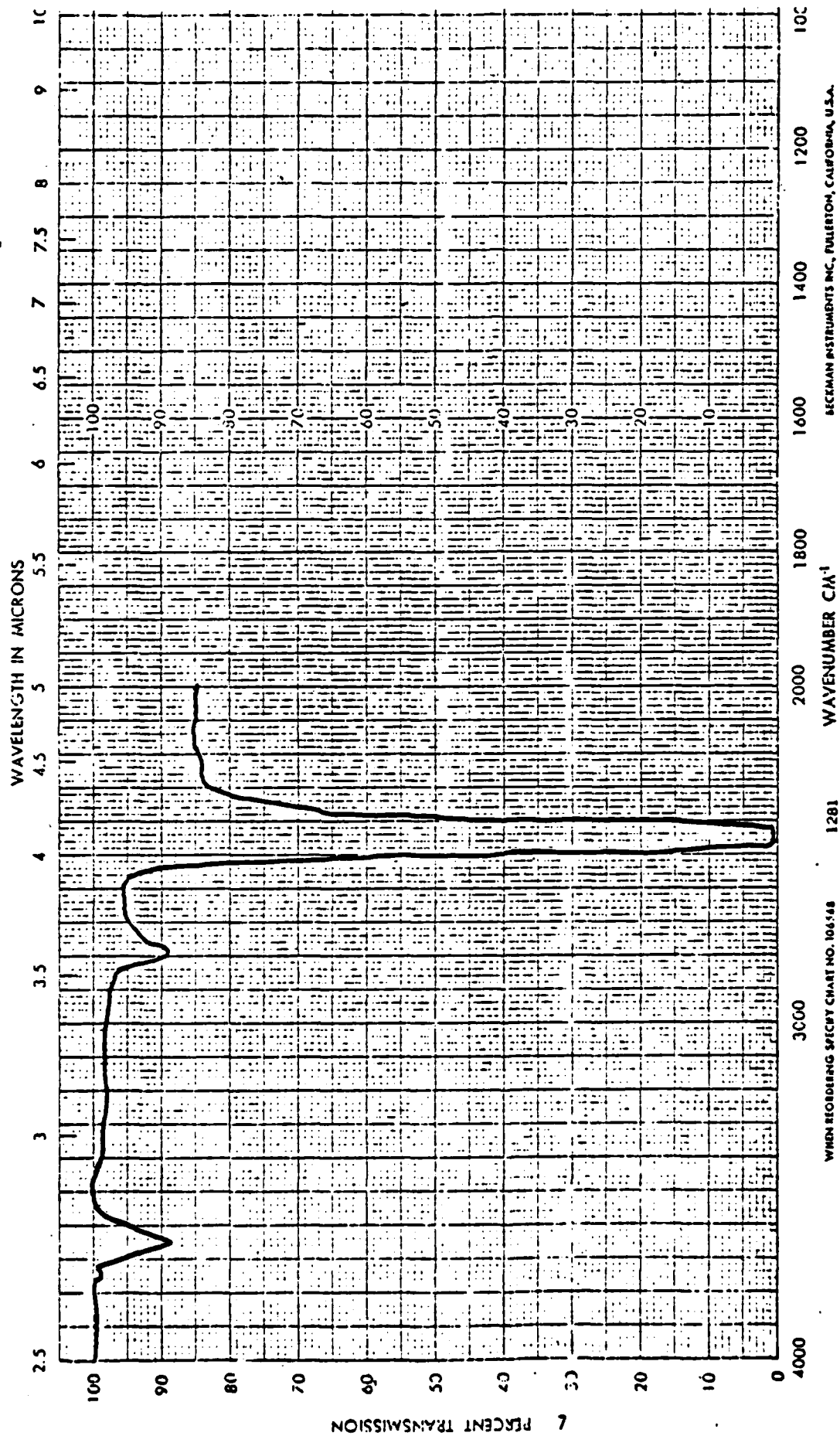


Figure 3. Eastman  $\text{SOCl}_2$

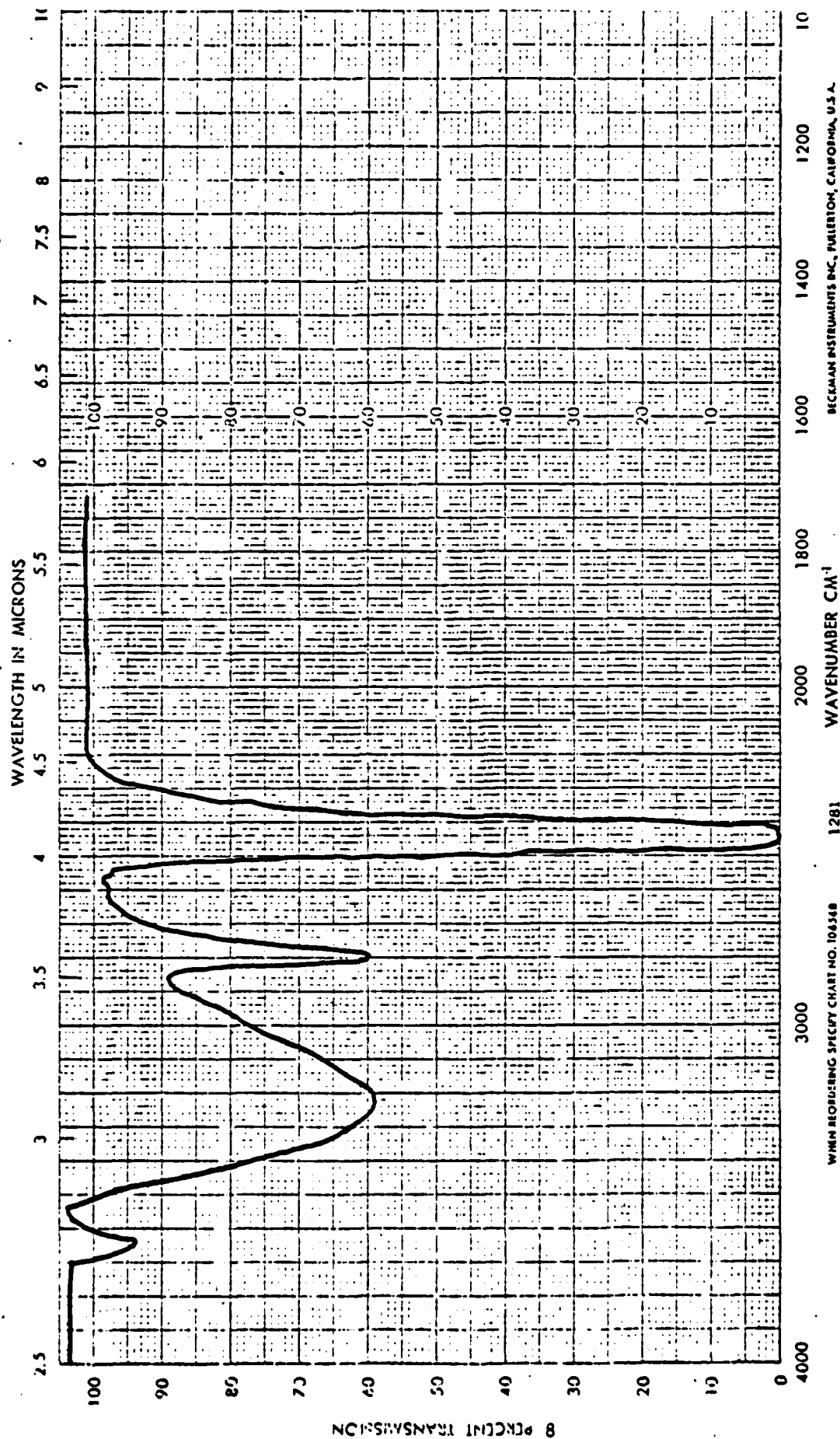


Figure 4. Fluka SOCl<sub>2</sub>

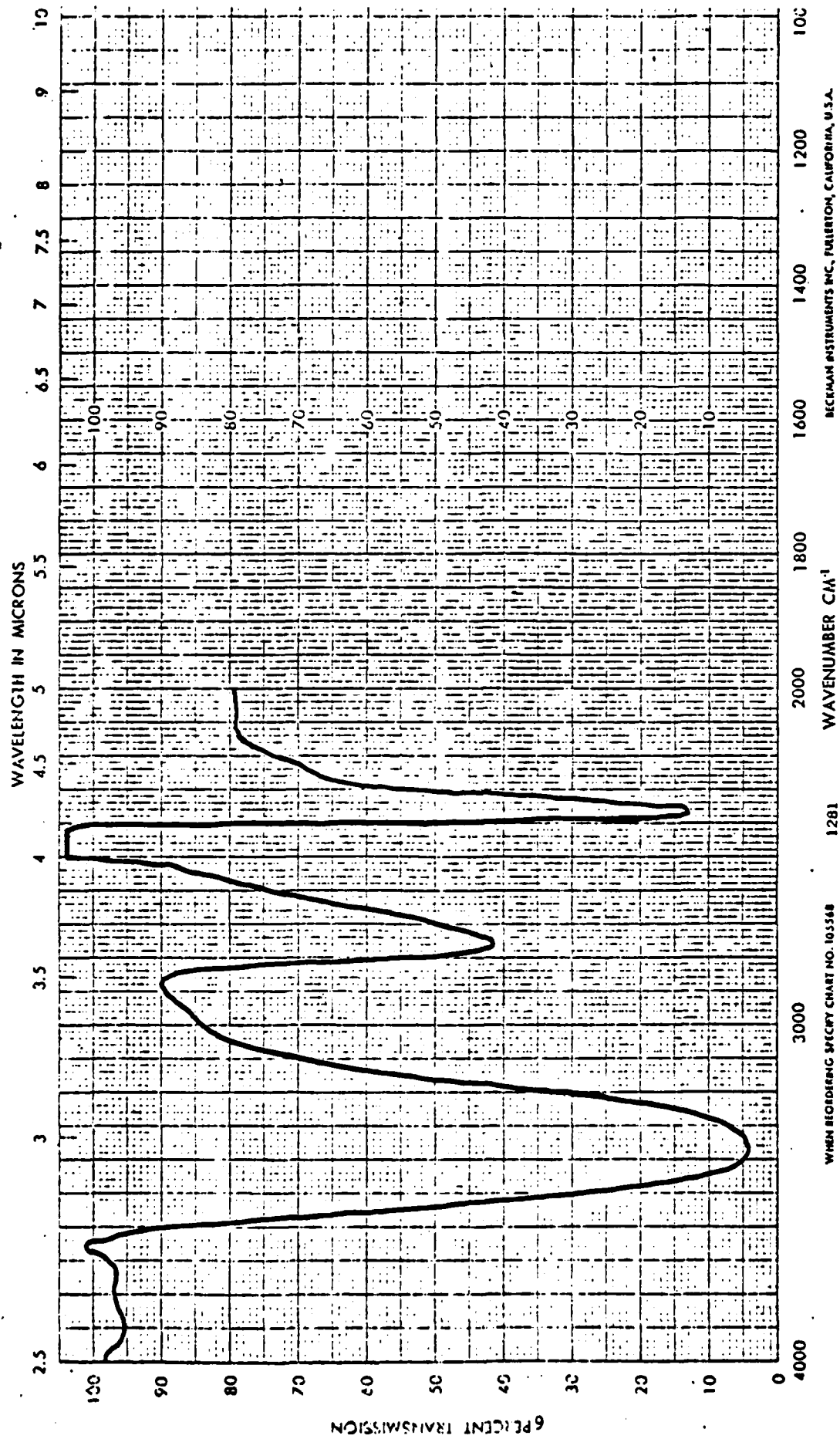


Figure 5. 1.5M  $\text{LiAlCl}_4$  from  $\text{AlCl}_3 + \text{LiCl}$

resulting electrolyte produced the spectrograph in Figure 6. This spectrograph indicates the electrolyte contains lower contaminant concentrations than the electrolytes represented in Figures 3, 4, and 5.

#### Separator Materials

Four separator materials have been evaluated in this program. Manning Paper Co. supplied two non-woven glass separators, one with binder and one without binder. The third material, manufactured by the Zicar Company, Florida, N.Y. was an yttria oxide base, non-woven separator with a binder. Initial testing consisted of thionyl chloride compatibility tests. C.H. Dexter Co. also supplied a non-woven glass separator without binder.

#### Storage Tests

Combinations of various cell components, additives, and contaminants were sealed in glass ampoules and stored at elevated temperatures. Glass ampoules resistant to thionyl chloride were cleaned and dried prior to filling and sealing. Following filling and sealing the ampoules were placed in hot storage and observed at regular intervals. The components in any ampoule were considered incompatible when either of the following changes were observed: 1) Electrolyte color or clarity, 2) calcium pitting or corrosion. Three ampoule tests have been constructed with a fourth test under design.

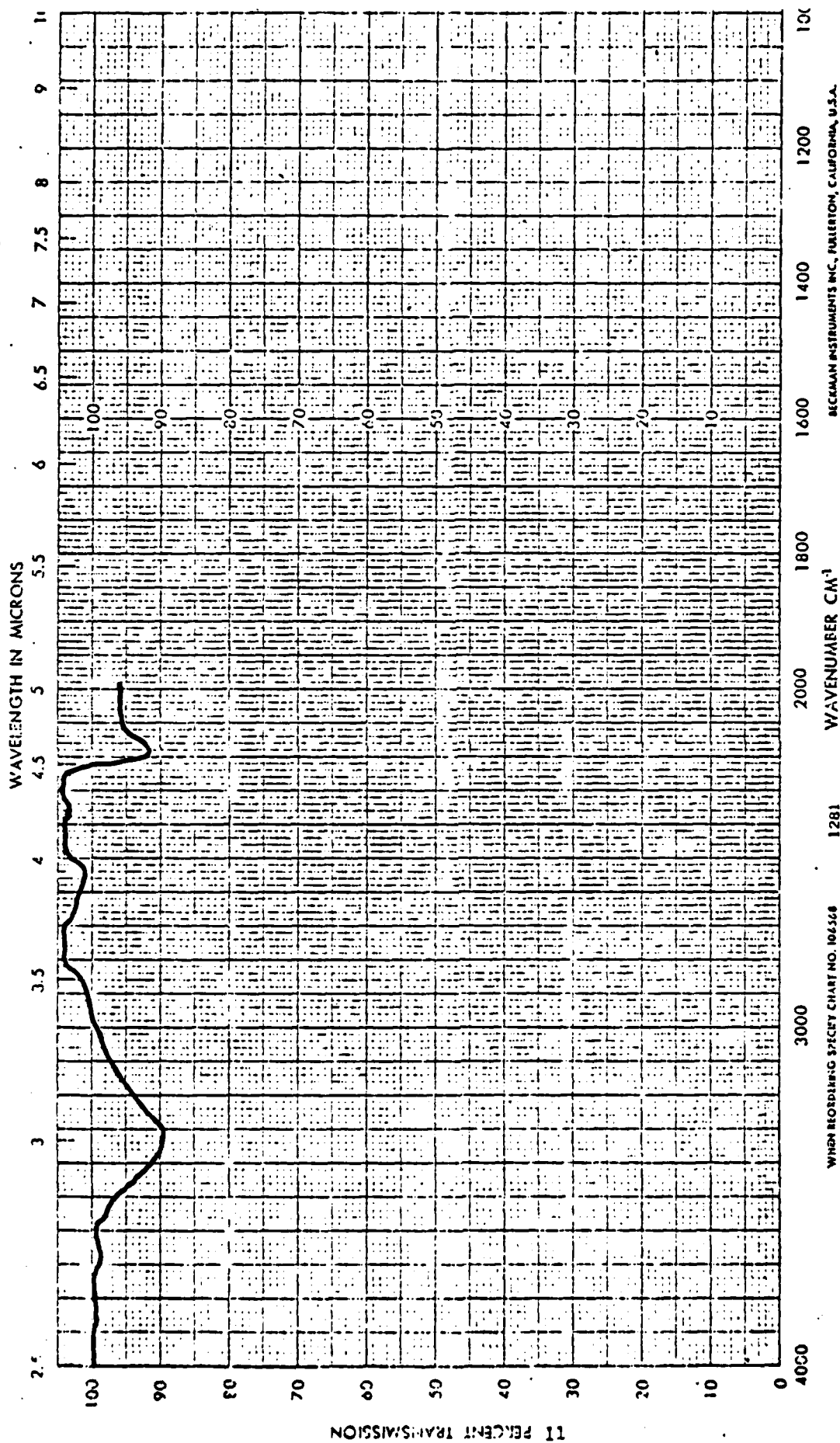


Figure 6. 1.5 LiAlCl<sub>4</sub> from Sublimed and Dried Salts

Tables 1, 2, and 3 list all materials and combinations used in the first ampoules test at +55C. Table 1 shows how 99% purity Pfizer calcium, 99.99% purity Alfa calcium, Manniglass separator with binder, and yttria oxide separator have each reacted with thionyl chloride solvent or electrolyte. Lithium, magnesium and aluminum were tested for comparison. Ampoules containing calcium and thionyl chloride doped with 5% water (H<sub>2</sub>O) and 5% sulfur have stored for 23 weeks with no indications of corrosion or chemical changes. Ampoules containing 1.5 LiAlCl<sub>4</sub> electrolyte produced calcium corrosion after 6 weeks of storage. This same electrolyte caused the binder in the Manniglass separator to react with the electrolyte. Lithium, however, has stored 23 weeks in the electrolyte before the surface color had turned dark gray in color. The yttria oxide separator was not affected.

Ampoules containing 0.5M Ca(AlCl<sub>4</sub>)<sub>2</sub> electrolyte resulted in calcium corrosion after 1 week of storage. Lithium corroded after 2 weeks of storage. This electrolyte also caused the Manniglass binder to dissolve. Yttria oxide has not been affected.

As a possible alternate solvent, sulfuryl chloride was evaluated in the storage test. Table 2 shows calcium, lithium, magnesium, aluminum, Manniglass with binder, and yttria oxide separator to be unaffected by the sulfuryl chloride solvent. Addition of either LiAlCl<sub>4</sub> or Ca(AlCl<sub>4</sub>)<sub>2</sub> resulted in ampoule failure in all cases except the yttria oxide separator. In most cases failure was observed after 2 weeks of storage.

Table 1. Ampoule Storage Test (Trial I)

START AT 130 F	AMPULE COMPONENTS	PASS/FAIL	E.T. (WEEKS)	ID
5-14-82	SOCl <sub>2</sub> (Eastman)			
	Ca (Pfizer)	Pass	23	1-1
	Ca (Alfa)	Pass	23	1-2
	Li	Pass	23	1-4
	Mg	Pass	23	1-5
	Al	Pass	23	1-6
	Manniglass (1400 with binder)	Pass	23	1-8
	Yttria Oxide	Pass	23	1-9
5-14-82	SOCl <sub>2</sub> + 5% Sulfur (Eastman)			
	Ca (Pfizer)	Pass	23	2-1
	Ca (Alfa)	Pass	23	2-2
	Li	Pass	23	2-4
	Mg	Pass	23	2-5
	Al	Pass	23	2-6
	Manniglass (1400 with binder)	Pass	23	2-8
	Yttria Oxide	Pass	23	2-9
5-14-82	SOCl <sub>2</sub> + 5% H <sub>2</sub> O (Eastman)			
	Ca (Pfizer)	Pass	23	3-1
	Ca (Alfa)	Pass	23	3-2
	Li	Pass	23	3-4
	Mg	Pass	23	3-5
	Al	Pass	23	3-6
	Manniglass (1400 with binder)	Pass	23	3-8
	Yttria Oxide	Pass	23	3-0
5-14-82	SOCl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub> (Lithcoa)			
	Ca (Pfizer)	Fail	6	4-1
	Ca (Alfa)	Fail	6	4-2
	Li	Fail	23	4-4
	Mg	Fail	2	4-5
	Al	Fail	2	4-6
	Manniglass (1400 with binder)	Fail	2	4-8
	Yttria Oxide	Pass	23	4-9
5-14-82	SOCl <sub>2</sub> + 0.5M Ca (AlCl <sub>4</sub> ) <sub>2</sub> (E-P)			
	Ca (Pfizer)	Fail	1	5-1
	Ca (Alfa)	Fail	1	5-2
	Li	Fail	2	5-4
	Mg	Fail	2	5-5
	Al	Fail	2	5-6
	Manniglass (1400 with binder)	Fail	2	5-8
	Yttria Oxide	Pass	23	5-9



Table 1. Ampoule Storage Test (Trial I)

START AT 130 F	AMPULE COMPONENTS	PASS/FAIL	E.T. (WEEKS)	ID
5-14-82	SO <sub>2</sub> Cl <sub>2</sub> (Eastman)	Pass	23	6-1
	Ca (Pfizer)	Pass	23	6-2
	Ca (Alfa)	Pass	23	6-4
	Li	Pass	23	6-5
	Mg	Pass	23	6-6
	Al	Pass	23	6-8
	Manniglass (1400 with binder)	Pass	23	6-9
	Yttria Oxide	Pass	23	6-9
5-14-82	SO <sub>2</sub> Cl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub> (E-P)	Fail	1	9-1
	Ca (Pfizer)	Fail	1	9-2
	Ca (Alfa)	Fail	2	9-4
	Li	Fail	2	9-5
	Mg	Fail	2	9-6
	Al	Fail	2	9-8
	Manniglass (1400 with binder)	Fail	2	9-8
	Yttria Oxide	Pass	23	9-9
5-14-82	SO <sub>2</sub> Cl <sub>2</sub> + 0.5M Ca (AlCl <sub>4</sub> ) <sub>2</sub> (E-P)	Fail	1	10-1
	Ca (Pfizer)	Fail	1	10-2
	Ca (Alfa)	Fail	2	10-4
	Li	Fail	2	10-5
	Mg	Fail	2	10-6
	Al	Fail	2	10-8
	Manniglass (1400 with binder)	Fail	2	10-8
	Yttria Oxide	Pass	23	10-9
5-24-82	SO <sub>2</sub> Cl <sub>2</sub> (Fluka)	Pass	23	15-1
	Ca (Pfizer)	Pass	23	15-2
	Ca (Alfa)	Pass	23	15-3
	Ca (PF 99.97)	Pass	23	15-4
	Li	Pass	23	15-5
	Mg	Pass	23	15-6
	Al	Pass	23	15-7
	Ca:Li (90:10 Alfa)	Pass	23	15-8
	Manniglass (1400 with binder)	Pass	23	15-9
5-24-82	Ca (PF 99.97)	Pass	21	1-3
	SOCl <sub>2</sub>	Pass	21	2-3
	SOCl <sub>2</sub> + 5% Sulfur	Pass	21	3-3
	SOCl <sub>2</sub> + 5% H <sub>2</sub> O	Fail	6	4-3
	SOCl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub> (Lithcoa)	Fail	1	5-3
	SOCl <sub>2</sub> + 0.5M Ca(AlCl <sub>4</sub> ) <sub>2</sub>	Pass	21	6-3
	SO <sub>2</sub> Cl <sub>2</sub> (Eastman)	Fail	1	9-3
	SO <sub>2</sub> Cl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub>	Fail	1	10-3

Table 1. Ampoule Storage Test (Trial I)

START AT 130 F	AMPULE COMPONENTS	PASS/FAIL	E.T. (WEEKS)	ID
5-24-82	Ca:Li (90:10 Alfa)			
	SOCl <sub>2</sub> (Eastmah)	Pass	21	1-7
	SOCl <sub>2</sub> + 5% S	Pass	21	2-7
	SOCl <sub>2</sub> + 5% H <sub>2</sub> O	Pass	21	3-7
	SOCl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub> (Lithcoa)	Fail	1	4-7
	SOCl <sub>2</sub> + 0.5M Ca (AlCl <sub>4</sub> ) <sub>2</sub>	Fail	1	5-7
	SO <sub>2</sub> Cl <sub>2</sub>	Pass	21	6-7
	SO <sub>2</sub> Cl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub>	Fail	1	9-7
	SO <sub>2</sub> Cl <sub>2</sub> + 0.5M Ca(AlCl <sub>4</sub> ) <sub>2</sub>	Fail	1	10-7
5-24-82	Dexter (without binder)			
	SOCl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub> (Lithcoa)	Pass	21	4-10
	SOCl <sub>2</sub> + 0.5M Ca(AlCl <sub>4</sub> ) <sub>2</sub>	Pass	21	5-10
	SO <sub>2</sub> Cl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub>	Pass	21	5-10
	SO <sub>2</sub> Cl <sub>2</sub> + 0.5M Ca(AlCl <sub>4</sub> ) <sub>2</sub>	Pass	21	10-10
6-21-82	SOCl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub>			
	Ca	Fail	6	1
	Ca (w/Cyanoacrylate Film)	Fail	6	3
	Manniglass (without binder)	Pass	19	5
6-21-82	SOCl <sub>2</sub> + 0.5M Ca(AlCl <sub>4</sub> ) <sub>2</sub>			
	Ca	Fail	1	2
	Ca (w/Cyanoacrylate Film)	Fail	1	4
	Manniglass (without binder)	Pass	19	6
7-13-82	SOCl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub>	Fail	2	-
	SOCl <sub>2</sub> + 1.0M Ca(AlCl <sub>4</sub> ) <sub>2</sub>	Fail	2	-
	SO <sub>2</sub> Cl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub>	Fail	2	-
	SO <sub>2</sub> Cl <sub>2</sub> + 0.5M Ca(AlCl <sub>4</sub> ) <sub>2</sub>	Fail	2	-
7-16-82	SOCl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub>	Fail	6	A
	SOCl <sub>2</sub> + 1.0M LiAlCl <sub>4</sub>	Fail	6	B
	SOCl <sub>2</sub> + 0.5M LiAlCl <sub>4</sub>	Fail	6	C
8-25-82	SOCl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub> + Ca (PF 99.97) +			
	Cobalt Phthalocyanine	Fail	5	-
	Iron Phthalocyanine	Fail	5	-
	Lithium Perchlorate	Fail	1	-
	Rhodium on Carbon Black	Fail	1	-
	Tetra Ethyl Ammonium Perchlorate	Fail	1	-
	Mg Perchlorate	Fail	1	-

Table 3 shows that an alloy containing 90% calcium and 10% lithium was corrosion resistant in sulfuryl chloride and thionyl chloride. Corrosion was observed after 1 week when the alloy was stored  $\text{LiAlCl}_4$  or  $\text{Ca}(\text{AlCl}_4)_2$  electrolytes. The Dexter glass separator without binder was inert to  $\text{LiAlCl}_4$  and  $\text{Ca}(\text{AlCl}_4)_2$  electrolytes.

Ampoule No's 1 and 3 (Table #3) show that cyanoacrylate film did not lengthen the storage time of calcium in  $1.5\text{M}$   $\text{LiAlCl}_4$ . The cyanoacrylate film was formed by successively dipping polished calcium foil into a solution of methylethylketone and cyanoacrylate ester until a .003 inch thick film had formed on each side of the calcium foil. The calcium and  $1.5\text{M}$   $\text{LiAlCl}_4$  electrolyte was sealed within an ampoule.

Two calcium alloys, one containing 10% aluminum and the other containing 10% copper, both failed at resisting corroding in either  $1.5\text{M}$   $\text{LiAlCl}_4$  electrolyte or  $0.5\text{M}$   $\text{Ca}(\text{AlCl}_4)_2$  electrolyte. Electrolytes using either thionyl chloride or sulfuryl chloride were used. In all cases, storage lasted no longer than 2 weeks before corrosion was observed.

Specimens A, B, and C in Table 3 show Pfizer calcium of 99.97% purity to store for no more than 6 weeks in  $1.5\text{M}$   $\text{LiAlCl}_4$  electrolyte. Pfizer calcium having 99% purity, sample 4-1 in Table 1, also stored for no more than 6 weeks in  $1.5\text{M}$   $\text{LiAlCl}_4$ .

The materials cobalt phthalocyanine, iron phthalocyanine, lithium perchlorate, rhodium-on-carbon black, tetraethylammonium-perchlorate, and magnesium, perchlorate were believed to be conductivity enhancers, passive layer formers, or catalysts. Their compatibility in 1.5M  $\text{LiAlCl}_4$  electrolyte along with 99.97% purity Pfizer calcium is shown in Table 3. There was no additive which could improve or equal the storage time of 6 weeks, as seen with ampoule 4-1 in Table 1.

Table 4 summarizes a second storage test at +55°C. Ampoules 7, 11 and 15 were exposed to 5% R.H. air for 1, 4, and 8 minutes respectively (in order to increase the hydrolysis contamination.) Figures 7, 8, and 9 show spectrographs of hydrolysis contamination. In all cases calcium corrosion was observed after no more than 4 weeks of storage. Typical storage time for calcium in 1.5M  $\text{LiAlCl}$  with minimum hydrolysis contamination has been 6 weeks.

Table 4 ampoule Nos. 19, 20, and 21 show the use of  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$  as an alternate electrolyte salt failed to increase the storage time over 1.5M  $\text{LiAlCl}_4$ , likewise the use of 1.2M  $\text{LiGaCl}_4$ , Table 4, failed to improve the storage time.

Since the presence of unreacted  $\text{AlCl}_3$  in the electrolyte may be causing the corrosion, an ampoule containing excess  $\text{LiCl}$  was constructed in order to determine if excess  $\text{LiCl}$  would inhibit the corrosion. Ampoule No. 38 in Table 4 shows that calcium corrosion was again observed after 7 weeks of storage. Calcium corrosion in

Table 4. Ampoule Storage Test (Trial II)

START AT 130 F	AMPULE COMPONENTS	PASS/FAIL	E.T. (WEEKS)	ID
11-3-82	Ca + 1.5M LiAlCl <sub>4</sub> + SOCl <sub>2</sub> (Ca polished)	Fail	6	3
11-3-82	Ca + 1.5M LiAlCl <sub>4</sub> + SOCl <sub>2</sub> 1 min. to air	Fail	4	7
11-3-82	Ca + 1.5M LiAlCl <sub>4</sub> + SOCl <sub>2</sub> 4 min. to air	Fail	4	11
11-3-82	Ca + 1.5M LiAlCl <sub>4</sub> + SOCl <sub>2</sub> 8 min. to air	Fail	4	15
11-3-82	Ca + 1.0M Li <sub>2</sub> B <sub>10</sub> Cl <sub>10</sub> + SOCl <sub>2</sub> (Ca unpolished)	Fail	7	19
11-4-82	Ca + 0.17M Li <sub>2</sub> B <sub>10</sub> Cl <sub>10</sub> + SOCl <sub>2</sub> (Ca unpolished)	Fail	7	20
11-4-82	Ca + 0.17M Li <sub>2</sub> B <sub>10</sub> Cl <sub>10</sub> + SOCl <sub>2</sub> (Ca polished)	Fail	7	21
11-12-82	Ca + 1.5M LiAlCl <sub>4</sub> + SOCl <sub>2</sub> (Ca polished)	Fail	7	22
11-12-82	Ca + 1.5M LiAlCl <sub>4</sub> + SOCl <sub>2</sub> (Ca unpolished)	Fail	7	26
11-15-82	Ca + 1.2M LiGaCl <sub>4</sub> + SOCl <sub>2</sub> (Ca unpolished)	Fail	7	30
11-23-82	Ca + 1.5M LiAlCl <sub>4</sub> + SOCl <sub>2</sub> (Ca polished)	Fail	7	34
11-23-82	Ca + 1.5M LiAlCl <sub>4</sub> + SOCl <sub>2</sub> (Ca unpolished) excess LiCl	Fail	7	22
Ca	Annealed Ca supplied by Pfizer			
AlCl <sub>3</sub>	Sublimed by E.P.I.			
LiCl	Dried at 160°C 7 x 10 <sup>-3</sup> mm Hg for 16 hours			
GaCl <sub>3</sub>	As received from Aldrich Chemical Company			
SOCl <sub>2</sub>	As received from Eastman Kodak			
Li <sub>2</sub> B <sub>10</sub> Cl <sub>10</sub>	Dried at 160°C 7 x 10 <sup>-3</sup> mm Hg for 16 hours			

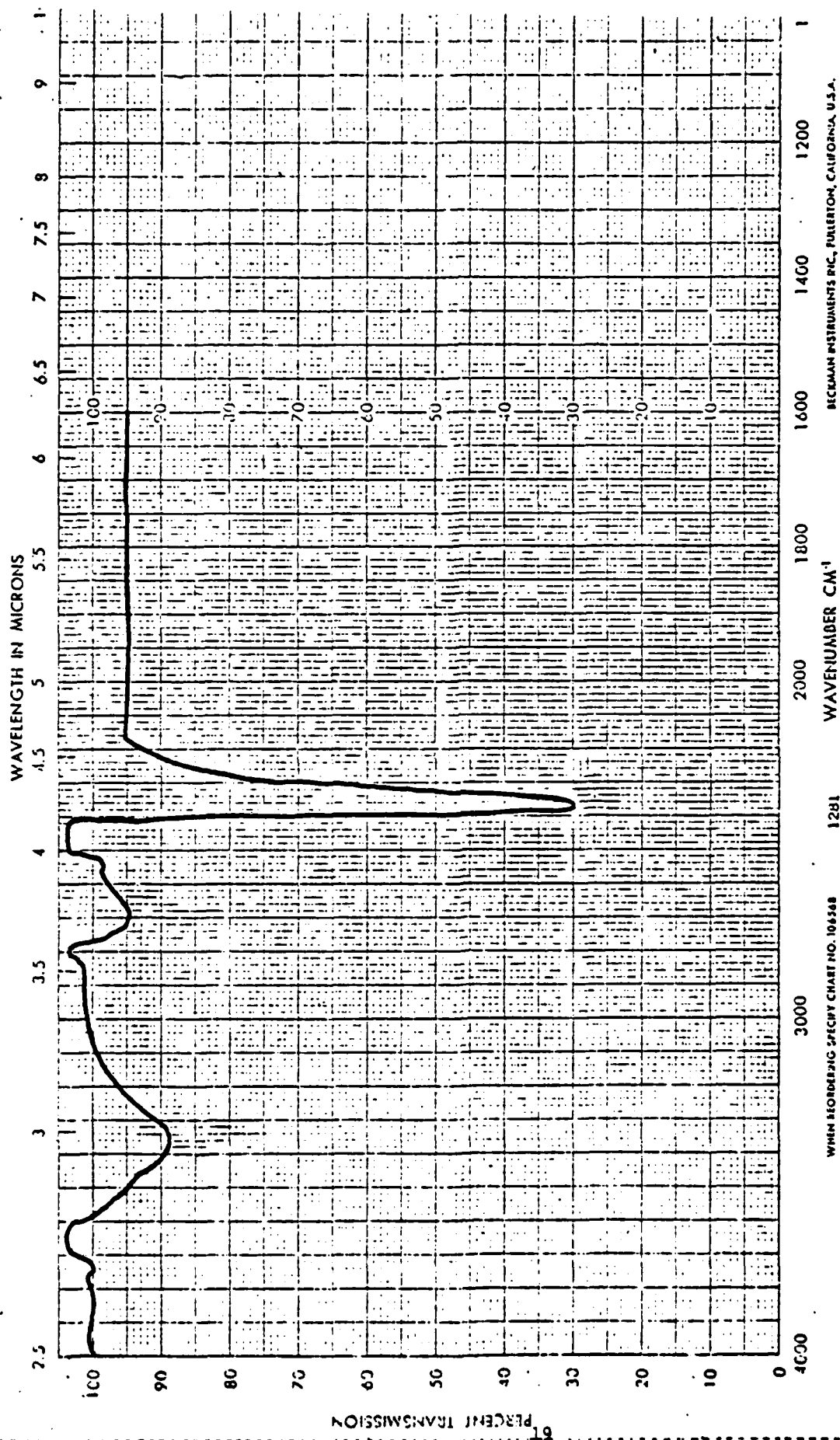


Figure 7. Lithcoa 1.5M LiAlCl<sub>4</sub> before Exposure to Air

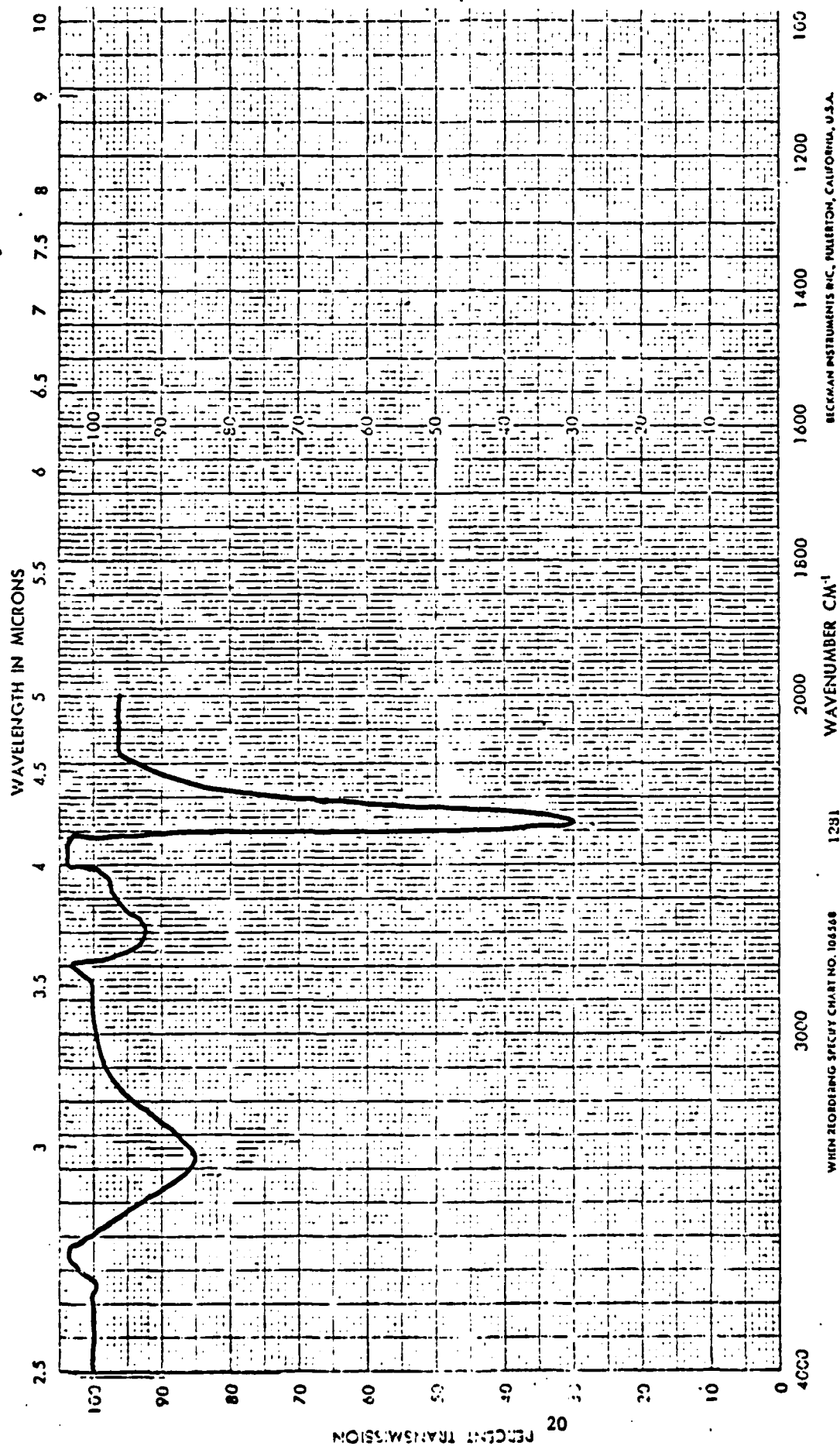


Figure 8. Lithcoa 1.5M LiAlCl<sub>4</sub> after 4 Minute Exposure to Air

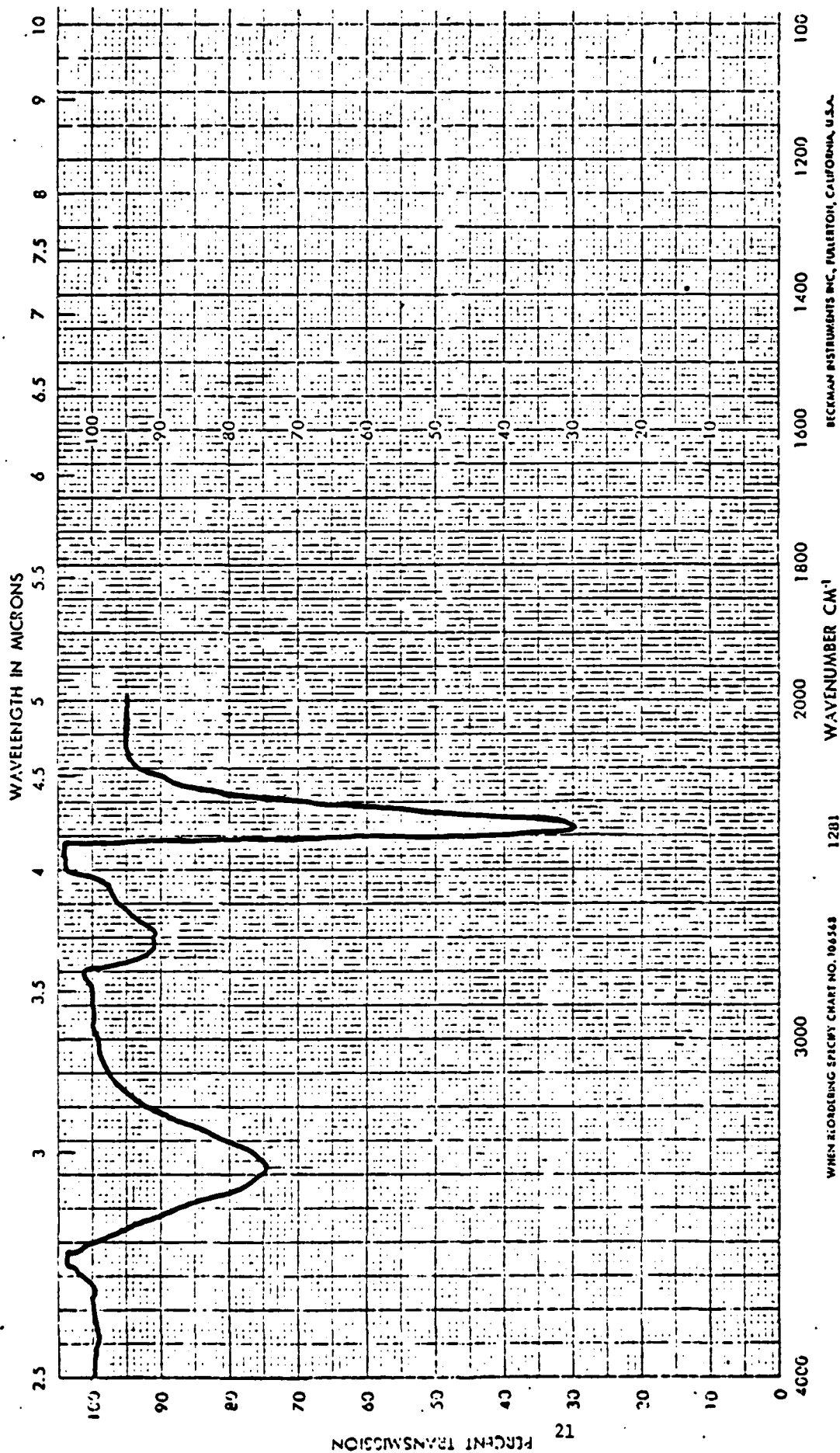


Figure 9. Lithocra P-5M LiAlCl<sub>4</sub> After 8 Minute Exposure to Air



1.5M  $\text{LiAlCl}_4$  appears to be independent of surface preparation since polished and unpolished calcium both store for approximately 7 weeks, as shown by ampoule Nos. 22 and 26 in Table 4.

The materials and combinations of the third ampoule test are listed in Table 5. This storage test was at  $+75^\circ\text{C}$ . The results show that calcium in 1.5M  $\text{LiAlCl}_4$  electrolyte showed corrosion at 4 weeks. The use of  $\text{SO}_2$  and vinyl polymer additives did not retard the corrosion. Calcium and 0.15M  $\text{LiAlCl}_4$  electrolyte also showed corrosion at 4 weeks, indicating that a reduced  $\text{LiAlCl}_4$  concentration did not increase the storage time. Calcium with 1.5M  $\text{LiGaCl}_4$  and 1.14  $\text{Ca}(\text{GaCl}_4)_2$  both showed corrosion at 4 weeks.

The ampoules containing the  $\text{SO}_2$  and the vinyl polymer in thionyl chloride solvent produced no calcium corrosion after 4 weeks. Tetramethyl ammonium chloride electrolyte has produced no calcium corrosion and no discoloring in the ampoule. All components have remained in their original condition.

Electrolyte storage tests each containing a different separator material have shown that separator with binder is not compatible with the electrolyte. Tables 1 and 2 show yttria oxide separator to be compatible with oxyhalides and oxyhalide electrolytes for 23 weeks at  $+55^\circ\text{C}$ . However, this separator has very poor mechanical and handling properties due to its loosely bound fibers.

Table 5. Ampoule Storage Tests (Trial III)

START AT +75C	AMPULE COMPONENTS	PASS/FAIL	E.T. (WEEKS)	ID
1-31-83	Ca + SOCl <sub>2</sub>	Pass	4	54
1-31-83	Ca + SOCl <sub>2</sub> + 2.1% SO <sub>2</sub>	Pass	4	58
1-31-83	Ca + SOCl <sub>2</sub> + 8.3% SO <sub>2</sub>	Pass	4	62
1-31-83	Ca + SOCl <sub>2</sub> + 0.1% Vinyl Polymer	Pass	4	66
1-31-83	Ca + SOCl <sub>2</sub> + 0.5% Vinyl Polymer	Pass	4	70
1-31-83	Ca + SOCl <sub>2</sub> + 1.5M LiAlCl <sub>4</sub>	Fail	4	74
1-31-83	Ca + SOCl <sub>2</sub> + 2.1% SO <sub>2</sub> + 1.5M LiAlCl <sub>4</sub>	Fail	4	78
1-31-83	Ca + SOCl <sub>2</sub> + 8.3% SO <sub>2</sub> + 1.5M LiAlCl <sub>4</sub>	Fail	4	82
1-31-83	Ca + SOCl <sub>2</sub> + 0.1% Vinyl Polymer + 1.5M LiAlCl <sub>4</sub>	Fail	4	86
1-31-83	Ca + SOCl <sub>2</sub> + 0.5% Vinyl Polymer + 1.5M LiAlCl <sub>4</sub>	Fail	4	90
1-31-83	Ca + SOCl <sub>2</sub> + 0.15M LiAlCl <sub>4</sub>	Fail	4	94
1-31-83	Ca + SOCl <sub>2</sub> + 1.5M LiGaCl <sub>4</sub>	Fail	4	98
1-31-83	Ca + SOCl <sub>2</sub> + 1.14 M Ca(GaCl <sub>4</sub> ) <sub>2</sub>	Fail	4	102
1-31-83	Ca + SOCl <sub>2</sub> + 1.5M (CH <sub>3</sub> ) <sub>4</sub> NCI	Pass	4	106
1-31-83	Ca + SOCl <sub>2</sub> + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>3</sub> Cl	Fail	4	110
1-31-83	Ca + SOCl <sub>2</sub> + Hg + 1.5M LiAlCl <sub>4</sub>	Fail	4	114
	Ca                    99.97% Pfizer			
	LiAlCl <sub>4</sub> 1.5M in SOCl <sub>2</sub> Lithcoa			
	GaCl <sub>3</sub> Aldrich Chemical			
	SOCl <sub>2</sub> Eastman Kodak			
	SO <sub>2</sub> Matheson			
	Vinyl Polymer    Union Carbide			
	(CH <sub>3</sub> ) <sub>4</sub> NCI            Aldrich			
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>3</sub> Cl            Hexcel			

Two types of Manniglass separator were evaluated through storage tests listed in Figures 1, 2, and 3. Manniglass 1400 which contains a binder was found to be stable with oxyhalide solvents containing no salts. The presence of electrolyte salts in the solvent, however, produces a reaction with the binder. The Manniglass separator without the binder was found to be stable in thionyl chloride electrolytes containing either  $\text{LiAlCl}_4$  or  $\text{Ca}(\text{AlCl}_4)_2$  for 23 weeks at  $+55^\circ\text{C}$ . Both Manniglass separators have excellent handling and mechanical properties.

Compatibility tests using Dexter glass separator contains no binder and has stored with various thionyl chloride electrolytes for 21 weeks at  $+55^\circ\text{C}$ . The Dexter material also has excellent handling and mechanical properties.

#### Electrolyte Development

Further efforts to eliminate the calcium corrosion in the presence of aluminum chloride included the use of an alternate or additional electrolyte salt. Also considered was the use of an oxyhalide other than thionyl chloride or a co-solvent to use with an oxyhalide which might improve the solubility of noncorrosive salt. Oxyhalides considered were sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ), sulfur monochloride ( $\text{S}_2\text{Cl}_2$ ), and sulfur dichloride ( $\text{SCl}_2$ ). Co-solvents considered were acetone, dimethylsulfite, methylacetate, ethyl ether, carbon disulfide, benzene, carbon tetrachloride, and chloroform. Table 6 shows the co-solvent/oxyhalide compatibility matrix. Most materials

Table 6.

## CO-SOLVENT/OXYHALIDE MATRIX

	$\text{SOCl}_2$	$\text{SO}_2\text{Cl}_2$	$\text{SCl}_2$	$\text{S}_2\text{Cl}_2$
Acetone	M-D	D	D	D
DMSI	M	D	M	M
MeAcetate	M	M	M	M
Ethyl Ether	M	M	M	M
$\text{CS}_2$	M	M	M	M
$\text{C}_6\text{H}_6$	M	M	M	M
$\text{CCl}_4$	M	M	M	M
$\text{CHCl}_3$	M	M	M	M

M = Mixes

D = Decomposes

were miscible in all proportions. Acetone was found to decompose in all oxyhalides. Dimethylsulfite decomposed in sulfuryl chloride and was compatible with the other oxyhalides.

Table 7 summarizes the salt/solvent compatibility test. Two salts appeared to be likely replacements for the aluminum containing salts in the electrolyte. Lithium decachlorodecaborate ( $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ ) and benzyltrimethylammonium chloride ( $\text{C}_{10}\text{H}_{16}\text{NCl}$ ) were each soluble in oxyhalide solvents, particularly thionyl chloride. The benzyltrimethylammonium chloride failed a hot storage test with calcium metal at  $+75^\circ\text{C}$  as shown in Table 5. Lithium decachlorodecaborate also failed to improve calcium storage as shown in Table 4.

Materials considered to replace aluminum chloride, or to act as an inhibitor in the calcium corrosion mechanism are summarized in Table 8. Four Group III chlorides were mixed with thionyl chloride at room temperature. Of the group only gallium trichloride produced an electrolyte following the addition of lithium chloride to the solution. Table 4 shows that calcium storage in  $1.5\text{M}$   $\text{LiGaCl}_4$  was not improved over using  $1.5\text{M}$   $\text{LiAlCl}_4$ . The Group IVB and Group VB chlorides listed in Table 4 were found to readily dissolve in thionyl chloride to form 1.0 molar solutions. However, after 4 weeks of storage at  $+75^\circ\text{C}$ , only the  $\text{WCl}_5$  was found to be compatible with calcium. Electrical performance of ( $\text{WCl}_5 + \text{CaCl}_2$ ) electrolyte had not been evaluated.

Table 7.

## SALT/SOLVENT MATRIX

	CS <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	CCl <sub>4</sub>	CHCl <sub>3</sub>	Ethyl Ether	SOCl <sub>2</sub>	SO <sub>2</sub> Cl <sub>2</sub>	SCl <sub>2</sub>	S <sub>2</sub> Cl <sub>2</sub>
Ca(BF <sub>4</sub> ) <sub>2</sub>	I	I	I	I	I	I	I	I	I
CaBr <sub>2</sub>	I	I	I	I	I	I	D	I	I
LiSCN	I	I	I	I	MS	D	D	D	I.
Li <sub>2</sub> B <sub>10</sub> Cl <sub>10</sub>	I	I	I	I	SS	VS	VS	D	SS
LiAsF <sub>6</sub>	I	I	I	MS	VS	I	I	I	I
C <sub>10</sub> H <sub>16</sub> NCI	I	I	I	VS	I	VS	VS	VS	SS
LiBF <sub>4</sub>	I	I	I	I	SS	I	I	I	I
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	I	I	I	I	I	SS	I	I	I
LiNO <sub>3</sub>	I	I	I	I	I	D	I	I	SS
LiBr	I	I	I	I	SS	I	SS	I	I
MgClO <sub>4</sub>	I	I	I	I	SS	D	I	I	I

VS = Very soluble  
 MS = Moderately soluble  
 SS = Slightly soluble  
 I = Insoluble  
 M = Mixes  
 S = Separates  
 D = Decomposes

Tetramethylammoniumchloride  $\{(\text{CH}_3)_4\text{NCl}\}$  in thionyl chloride was found to be stable with calcium. Table 5 shows 1.5M  $(\text{CH}_3)_4\text{NCl}$  and calcium have stored for no less than four weeks at  $+75^\circ\text{C}$  with no calcium corrosion or electrolyte changes observed. The conductivity of thionyl chloride solutions containing  $(\text{CH}_3)_4\text{NCl}$  is shown in Figure 10. Also shown are the conductivities for solutions of  $\text{LiGaCl}_4$  and  $\text{LiAlCl}_4$ . While the conductivity of  $(\text{CH}_3)_4\text{NCl}$  at  $+20^\circ\text{C}$  is similar to  $\text{LiAlCl}_4$  solutions, the electrical performance of the two had not been evaluated.

Table 8 also lists materials which may act as corrosion inhibitors in the calcium/aluminum chloride electrolyte. Of the materials listed, formamide, tetramethylammoniumchloride, mercuric acetate, disodium ethylenediaminetetraacetate, potassium acetate, and sodium diethyldithiocarbamate all react with the  $\text{LiAlCl}_4$  electrolyte to form a heavy precipitate, making the use of these materials unlikely. Evaluation of the other materials had not been completed.

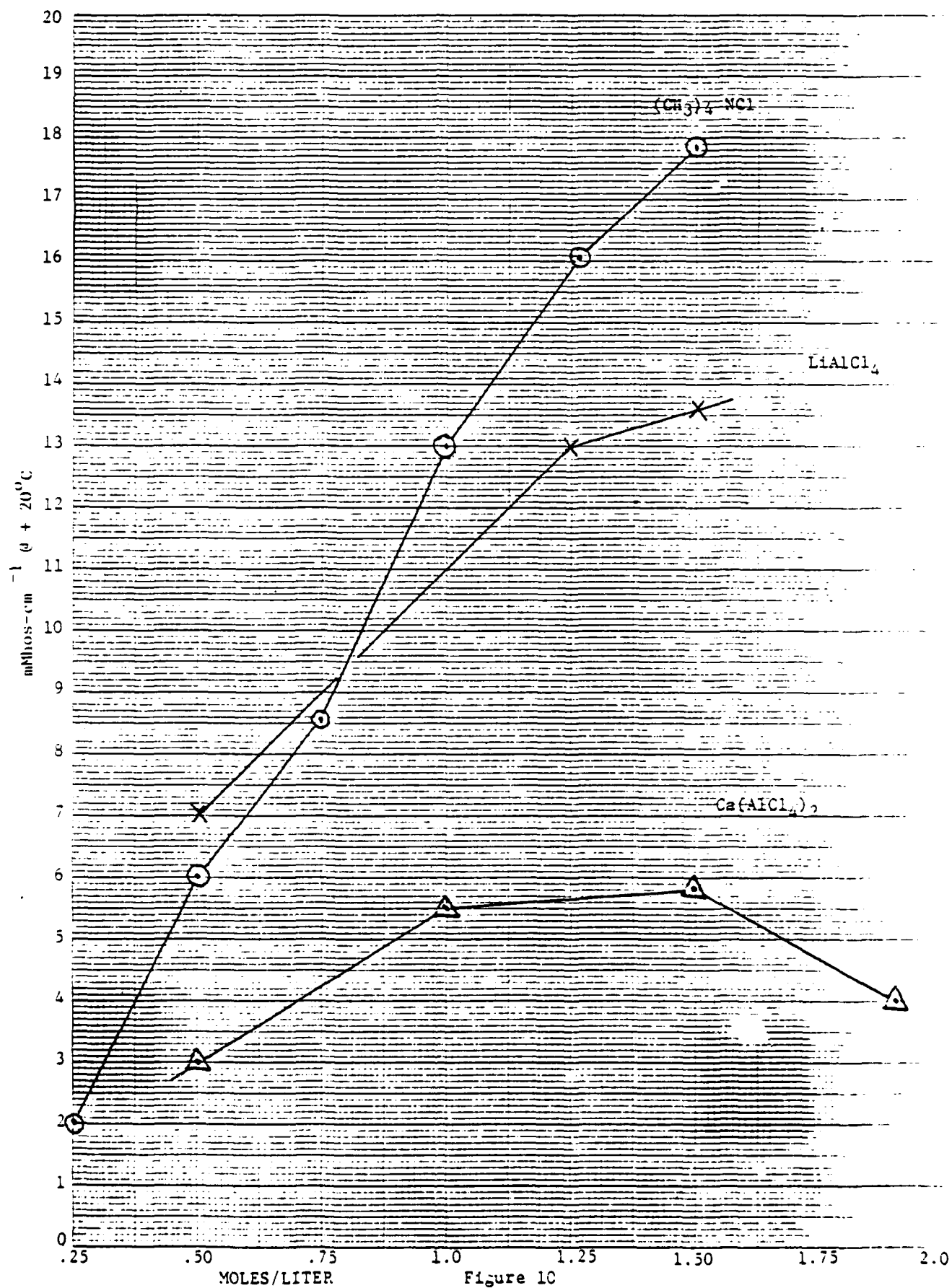


Figure 1C



TABLE 8

ELECTROLYTE SALTS AND INHIBITORSSALTS

$\text{BCl}_3$	$\text{SbCl}_5$
$\text{GaCl}_3$	$\text{PCl}_5$
$\text{InCl}_3$	$\text{WCl}_5$
$\text{TiCl}_3$	$\text{TaCl}_5$
$\text{CaS}$	$\text{NbCl}_5$
$(\text{CH}_3)_4\text{NCl}$	$\text{SiCl}_4$
$\text{SnCl}_2$	$\text{SnCl}_4$

Inhibitors

Formamide	Calcium Oxalate
Tetramethylammonium chloride	Calcium Acetate
Disodium Ethylenediaminetetraacetate	Calcium Propionate
Sodium Diethyldithiocarbamate	Propylene Oxide
Mercuric Acetate	Mesityl Oxide
Potassium Acetate	Mesitylene
Dimethyl Formamide	Diphenylamine
Calcium Stearate	Anthraquinone
	Arsenic III Chloride

### SECTION III

#### CORROSION STUDIES

An inert atmosphere glove box system was set up for the handling of calcium metal and thionylchloride solvent. The glove box is a Vacuum Atmospheres (VAC) Dri-Lab with the capability of maintaining an inert atmosphere with less than 10 ppm  $O_2$ ,  $H_2O$ , and  $N_2$ . Experimentation and sample preparation were normally carried out in atmospheres containing less than 100 ppm  $O_2$ , and  $H_2O$ . No attempt was made to remove  $N_2$  due to its low reactivity with Ca. The atmosphere in the box was periodically purged with dry argon and solvent vapors were removed by means of a liquid nitrogen cold trap. An auxiliary glove box was also set up for experimentation and sample preparation which does not require the stringent atmospheric control provided by the VAC system.

The electrochemical cell utilized in these studies was constructed of Pyrex glass and is comprised of two compartments. The main reaction chamber is cylindrical with an inner diameter of 3.8 cm. It is fitted with a top, via a ground glass fitting, which has an electrical feedthrough to a cylindrical shaped Pt gauze counter (auxiliary) electrode. The counter electrode is centered in the main reaction chamber with an opening along the length of one side. An opening in the top is sealed to a 6 mm i.d. glass tube through which the working electrode, described below, is inserted. A straight tubing coupler is used to seal the working electrode to the glass tubing.

The second chamber of the cell comprises the reference electrode compartment. It is formed by attachment of a side-arm tube to the main

chamber to a point very near the center. A AgCl coated Ag wire was used as the reference electrode.

The Ca metal working electrodes for insertion in the electrochemical cell were prepared from 1 inch diameter Ca metal rods obtained from Electronics Space Products, Inc. (854-56 S. Robertson Blvd., Los Angeles, California 90035). The purity was specified as 99.9% metals basis. The rods were reduced to 0.200 inch diameter on a lathe using a recirculating oil cooling system and very slow machining. There was no apparent work hardening during this process. The resulting rods, approximately 2 inches in length, were press fitted into an 0.250 inch o.d. Kel-F sheath and tapped on one end to accept a 4-40 thread. An 0.250 inch diameter brass rod, approximately 4 inches in length, was reduced to 0.200 inch diameter and tapped on one end to accept a 4-40 thread for electrical connection. The other end was fashioned with a 4-40 stud for attachment to the previously described Ca electrode. The brass rod was press fitted into a Kel-F sheath which was 0.250 inches o.d. on the lower 3 inches of its length and 5/16 inch o.d. on the remainder. This form allowed insertion into the cell and positioning via the tubing coupler at the top of the cell. The brass section of this two-part electrode is thus reusable, while the Ca surface may be renewed by either machining, polishing, or replacement. The exposed Ca surface area was  $0.21 \text{ cm}^2$ .

High-purity  $\text{SOCl}_2$  (Eastman Kodak),  $\text{AlCl}_3$  (J.T. Baker, anhydrous, powder), and  $\text{CaCl}_2$  (J.T. Baker, anhydrous, granular, 4 mesh) were dried where necessary and used without further purification. A supply of 1.8  $\text{M}$   $\text{LiAlCl}_4$  was provided by Lithcoa and was used as

received. The Ca electrodes were subjected to a surface preparation procedure to provide a reproducible surface prior to immersion in an electrolyte. Electrodes were treated prior to each electrochemical measurement, except those performed on electrodes subjected to storage tests. The surface preparation procedure consists of rough polishing with 400 grit polishing paper followed by final polishing with 600 grit paper. In both steps the paper is wetted with  $\text{SOCl}_2$  during polishing. Polishing is performed in the glove box.

A glass reaction vessel was designed and fabricated to facilitate the preparation of electrolyte solutions consisting of  $\text{SOCl}_2$ , electrolyte salts, and  $\text{AlCl}_3$ . The vessel consists of a round bottom flask with three ground glass joints. Two of these joints accommodate small side-arm vessels which contain the  $\text{AlCl}_3$  reactant. By rotation of the side-arm vessels, small additions of  $\text{AlCl}_3$  can be made, thus providing excellent control over the dissolution reaction. This technique, combined with immersion in an ice-water bath, allows the electrolyte to be prepared without over-heating.

All electrochemical experiments were performed using a Princeton Applied Research (PAR) Model 175 Universal Programmer and PAR Model 173 Potentiostat/Galvanostat for controlling the stimulus applied to the system under study. Responses were recorded on a Hewlett-Packard Model 7047A X-Y/T recorder. All experiments utilized a reference electrode to provide measurements of working electrode potential with as little contribution from uncompensated resistance effects as possible.

Several different electrochemical techniques were utilized during the course of this investigation. Each subjects the system under study to different stimuli, with responses controlled by various physical and electrochemical phenomena. A brief description of each of these techniques follows with a statement regarding their utility in the current application.

Potentiostatic Polarization - a technique in which the potential of the working electrode (Ca) is held constant while the current required to maintain that potential is monitored. In the case of metal dissolution, potentials anodic of the open circuit voltage are applied and the resulting anodic current is monitored. The current observed is determined in part by the rate of dissolution of the metal at the set potential and by the rate of diffusion of reactants to and from the metal surface. In this technique only those electrochemical processes which occur at potentials equal to or more cathodic than the set potential can occur. In the present application, this technique provides information regarding the ability of the metal in a particular electrolyte to provide current with fixed or limited polarization.

Galvanostatic Polarization - this technique is complementary to potentiostatic polarization. In this case, the current through the working electrode is maintained constant while its potential is monitored. The controlling processes are the same as before, except that the potential is free to shift to any process required to maintain the present current. Thus, the observed potential may represent a

mixed potential from several different processes. This technique provides information regarding the ability of the electrode in a particular electrolyte to maintain a constant current drain, wherein the cell potential may be of secondary importance.

Rapid Scan Chronopotentiometry - in this technique the current applied to the electrode is increased rapidly and the potential response of the electrode/electrolyte system is monitored. The rapidly changing current allows only those processes which can occur quickly to contribute to the observed potential. Thus, in the ideal case, the response should be identical to that observed for galvanostatic polarization. If, however, processes of varying speeds are occurring simultaneously, differences in the responses to the two techniques will be observed. Therefore, this technique provides information regarding the mechanism responsible for controlling the polarization and current delivering capability of a given system.

### Results

Figure 11 shows the variation of conductivity with respect to the concentration of  $\text{LiAlCl}_4$  and  $\text{Ca}(\text{AlCl}_4)_2$  in  $\text{SOCl}_2$ . Four  $\text{LiAlCl}_4$  and four  $\text{Ca}(\text{AlCl}_4)_2$  electrolytes were prepared for galvanostatic and chronopotentiometric polarization studies.

#### a). Mechanism of Anodic Dissolution by Rapid Scan Chronopotentiometric Polarization

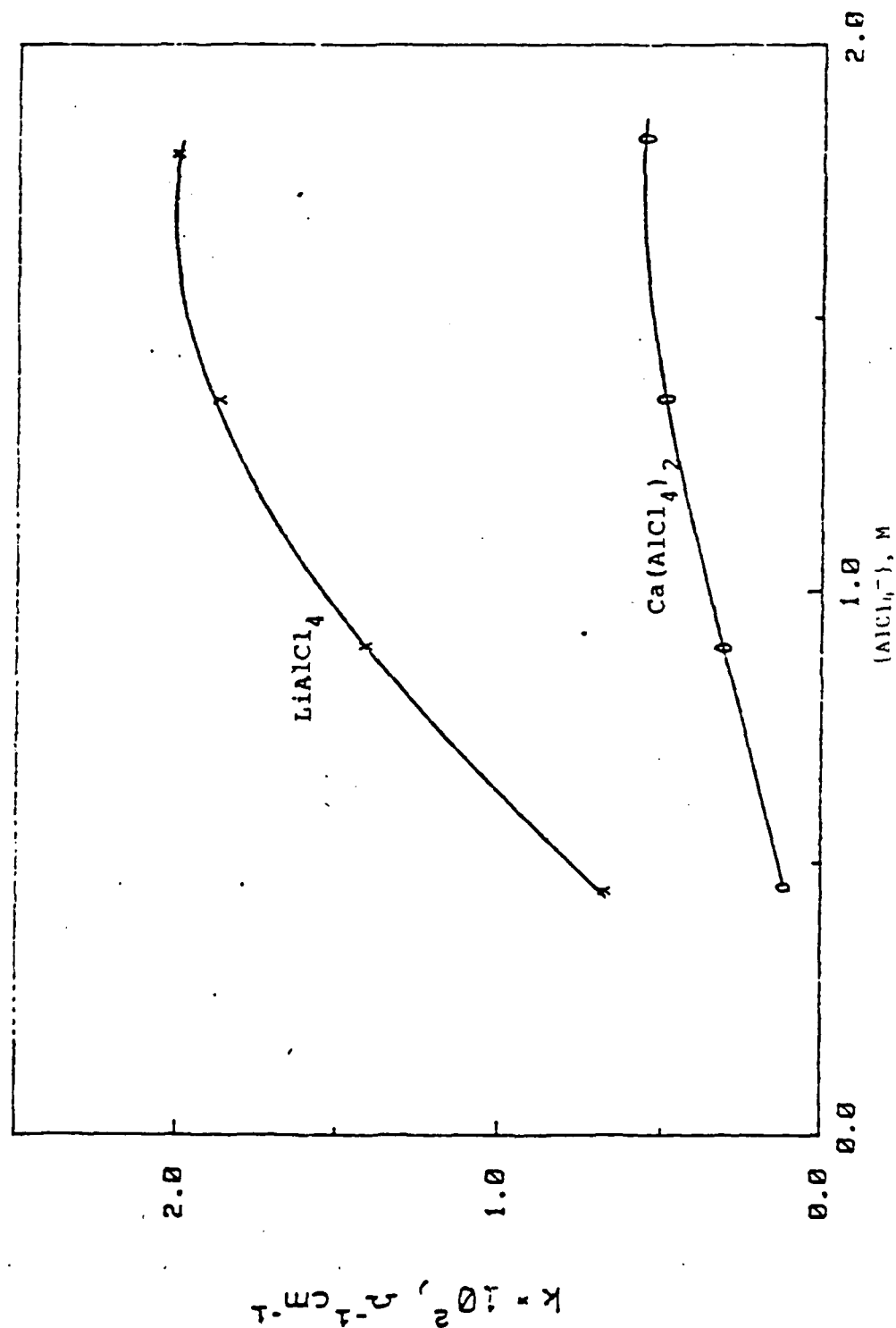
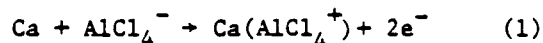


Figure 11. Variation of conductivity,  $k(\Omega^{-1} \text{cm}^{-1})$ , with respect to the concentration of  $\text{LiAlCl}_4$  and  $\text{Ca}(\text{AlCl}_4)_2$  in  $\text{SOCl}_2$

If the anodic dissolution of Ca is a single step reaction represented by  $\text{Ca} \rightarrow \text{Ca}^{++} + 2\text{e}^-$ , no effect of  $\{\text{AlCl}_4^-\}$  on the anodic polarization curve should be observed. This, however, does not agree with the results from this study. Figure 12 shows the chronopotentiometric polarization of Ca in  $\text{LiAlCl}_4$  electrolytes. Within the experimental error (i.e.,  $\pm 11\%$ ), the charge transfer reaction of Ca exhibits the same characteristics in various electrolytes, with Tafel slopes of  $\approx 126$  mV/decade. However, the rate of anodic dissolution of Ca in each electrolyte is different. To explain these results, a reaction involving  $\text{AlCl}_4^-$  ion is assumed for the anodic dissolution of Ca, that is



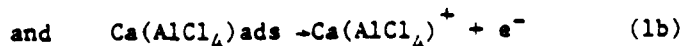
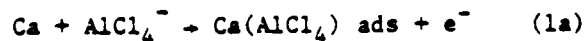
where  $\text{Ca}(\text{AlCl}_4)^+$  is a complex ion at the metal surface.

Based on electrokinetics, the rate of this reaction can be derived if the rate determining step is established. Thus, if Equation (1) is a single step reaction, the rate would be given by

$$i = k \{\text{AlCl}_4^-\} \exp\left(\frac{2\alpha F}{RT} \cdot \eta\right) \quad (2)$$

where  $k$  is a constant,  $\{\text{AlCl}_4^-\}$  is the concentration of  $\text{AlCl}_4^-$  and  $\eta$  is the overvoltage.

From the standpoint of kinetics, Equation (1) may be further divided into two consecutive elementary steps





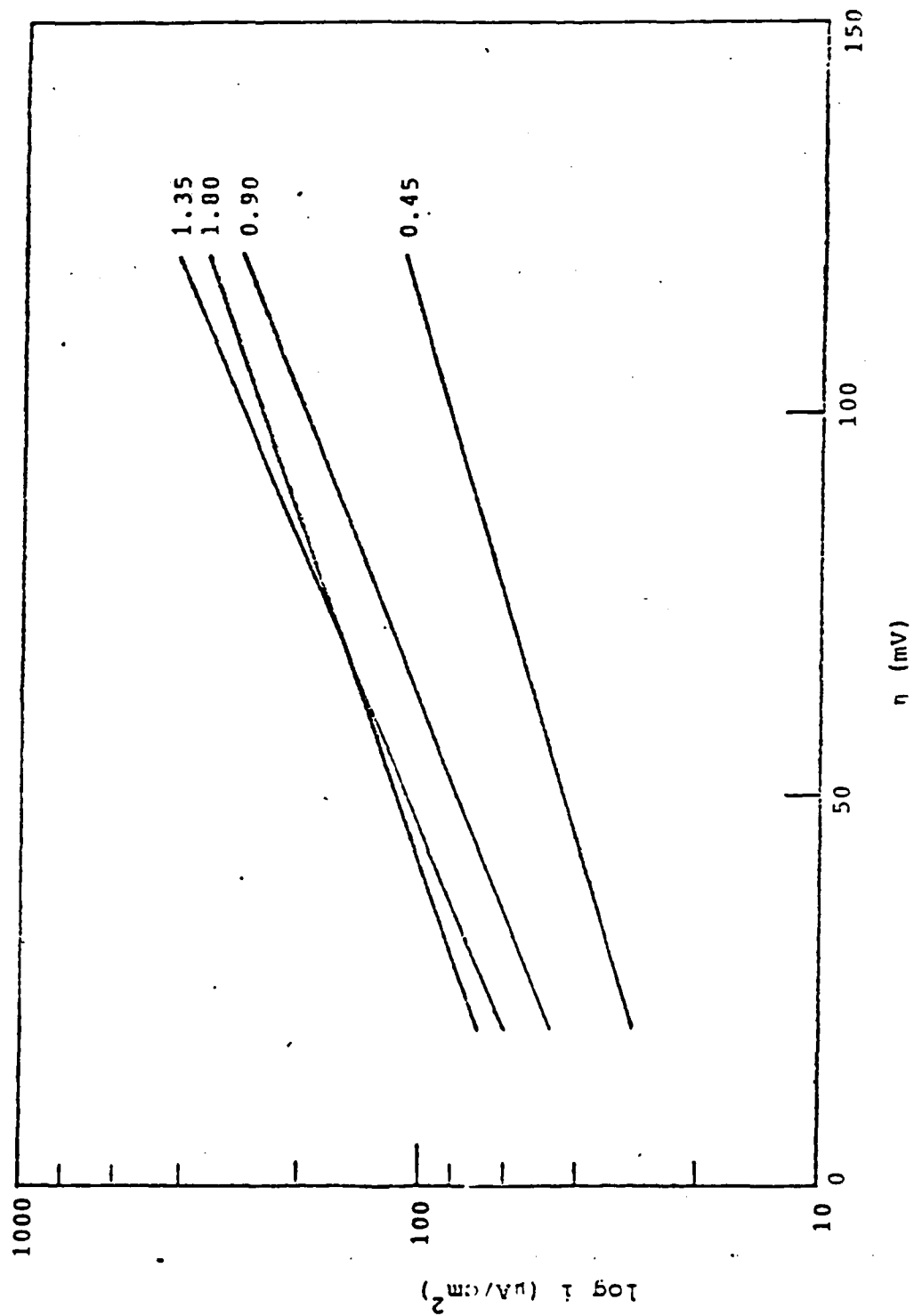


Figure 12. Rapid scan chronopotentiometric polarization of calcium in  $\text{LiAlCl}_4/\text{SOCl}_2$  electrolytes at room temperature. Sweep Rate:  $1\text{mA}/\text{second}$ .

where  $\text{Ca}(\text{AlCl}_4)_{\text{ads}}$  is an activated complex adsorbed on the metal surface.

For step (1a), the rate of overall reaction is given by

$$i = k_a \{\text{AlCl}_4^-\} \exp\left(-\frac{\alpha F}{RT} \cdot \eta\right) \quad (3)$$

where  $k_a$  is a constant.

If step (1b) is rate determining, the derivation of the rate equation for the overall reaction will lead to two different results depending upon whether  $\theta$ , the surface coverage of  $\text{Ca}(\text{AlCl}_4)_{\text{ads}}$ , is  $\theta \rightarrow 0$  or  $\theta \rightarrow 1$ . In both cases, the Langmuir adsorption isotherm can be applied.

The rate of step (1b) is then

$$i = k_b \{\text{Ca}(\text{AlCl}_4)_{\text{ads}}\} \exp\left(-\frac{\alpha F}{RT} \cdot \eta\right) \quad (4)$$

where  $k_b$  is a constant and  $\{\text{Ca}(\text{AlCl}_4)_{\text{ads}}\}$  is the concentration of adsorbed  $\text{Ca}(\text{AlCl}_4)$  on the surface.

Assuming that  $\theta = K \{\text{Ca}(\text{AlCl}_4)_{\text{ads}}\}$ , then

$$i = k_b' \theta \exp\left(-\frac{\alpha F}{RT} \cdot \eta\right) \quad (5)$$

where  $k_b' = K \cdot k_b$ .

Under conditions such that (1b) is the rate determining step, (1a) can be regarded as being in a quasi-equilibrium state when  $\theta \rightarrow 0$ . We may then, from the Langmuir isotherm, write

$$\{\text{Ca}(\text{AlCl}_4)_{\text{ads}}\} = k_a \{\text{AlCl}_4^-\} \exp\left(-\frac{F}{RT} \cdot \eta\right) \quad (6)$$

where  $k_a$  is a constant. Substitution of Equation (6) into Equation (4) gives the rate of overall reaction

$$i = k_a k_b \{AlCl_4^-\} \exp \frac{(1+\alpha)F}{RT} \cdot n) \quad (7)$$

When  $\theta \rightarrow 1$ , Equation (7) is no longer valid, and the rate is simply given by Equation (5), i.e.,

$$i = k_b' \exp \left( \frac{\alpha F}{RT} \cdot n \right) \quad (8)$$

Based on the rate expression given by Equations (2, 3, 7, and 8), the Tafel constant ( $\alpha n$ ), and the  $\{AlCl_4^-\}$  dependence of the reaction rate can be calculated for each reaction mechanism. Table 9 gives the results of these calculations.

By comparison of calculated results as shown in Table 9, one can verify the reaction mechanism. Figure 12 exhibits the polarization results by means of rapid scan chronopotentiometric results by means of rapid scan chronopotentiometric techniques. As we can see from this figure, each line corresponds to one concentration of  $AlCl_4^-$ . Within the experimental error of  $\pm 11\%$ , all lines are fairly parallel. The average Tafel slope of these lines is 126 mV/decade. This Tafel slope value corresponds to a one charge transfer reaction with  $\alpha = 0.5$ . In this case, reaction (1a) as shown in Table 9 is strongly favored for the anodic dissolution of calcium in  $LiAlCl_4/SOCl_2$  electrolytes when rapid scan chronopotentiometric polarization is employed.

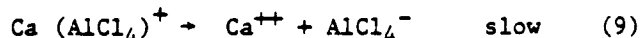
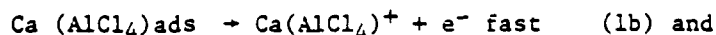
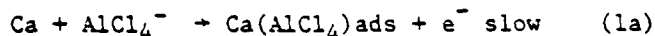
Table 9. Tafel Constant and  $(\text{AlCl}_4)^-$  Dependence of Anodic Dissolution of Calcium

Reaction Step	Tafel Constant* $\tau = n\alpha = \frac{RT}{F} \left( \frac{\partial \log i}{\partial \eta} \right)$	$(\text{AlCl}_4)^-$ dependence $= \left( -\frac{\partial \log i}{\partial \log(\text{AlCl}_4^-)} \right)$
$\text{Ca} \rightarrow \text{Ca}^{++} + 2e^-$	1	0
$\text{Ca} + \text{AlCl}_4^- \rightarrow \text{Ca}(\text{AlCl}_4)^+ + 2e^- \quad (2)$	1	1
$\text{Ca} + \text{AlCl}_4^- \rightarrow \text{Ca}(\text{AlCl}_4)_{\text{ads}} + e^- \quad (1a)$	0.5	1
$\text{Ca}(\text{AlCl}_4)_{\text{ads}} \rightarrow \text{Ca}(\text{AlCl}_4)^+ + e^- \quad (1b)$		
$0 \rightarrow 0$	1.5	1
$0 \rightarrow 1$	0.5	0

\* assuming  $\alpha = 0.5$

b. Mechanism of Anodic Dissolution by  
Galvanostatic Polarization

Galvanostatic polarization curves were obtained for Ca in both  $\text{LiAlCl}_4/\text{SOCl}_2$  and  $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$  electrolytes. Figure 13 shows the polarization of Ca in  $\text{LiAlCl}_4$  electrolytes. Although the Tafel slope values are scattered, ranging from 33 to 50 mV/decade, the polarization curves exhibit no dependency on the concentration of  $\text{AlCl}_4^-$ . By comparing Figures 12 and 13 and from Table 9, it can be seen that the rate-determining step of the anodic reaction is shifting from Equation (1a) to a pure charge transfer reaction, i.e.,  $\text{Ca} \rightarrow \text{Ca}^{++} + 2\text{e}^-$ , when the polarization format changes from rapid scan to steady-state. From previous results obtained for rapid scan polarization, it could be shown that the most probable mechanism for the steady-state anodic polarization of calcium in  $\text{LiAlCl}_4/\text{SOCl}_2$  electrolytes is



The results of galvanostatic polarization of Ca in  $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$  electrolytes is summarized in Figure 14. A careful examination of Figures 13 and 14 reveals that there are three distinct differences between the polarization characteristics of Ca in  $\text{LiAlCl}_4$  and  $\text{Ca}(\text{AlCl}_4)_2$  electrolytes. First, the Tafel slope of Ca in the calcium salt electrolyte is almost double that in

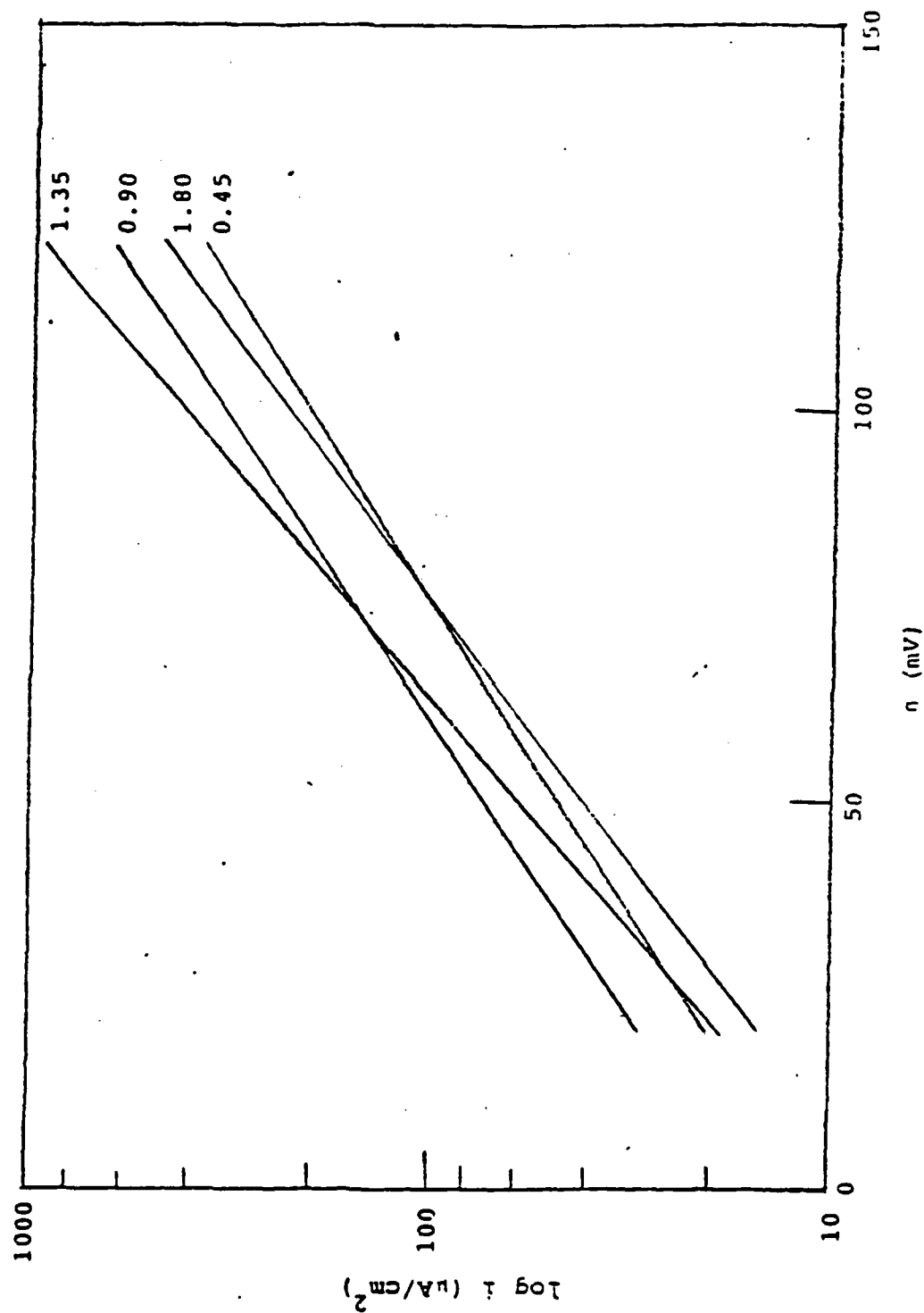


Figure 13. Galvanostatic polarization of calcium in  $\text{LiAlCl}_4/\text{SOCl}_2$  electrolyte at room temperature

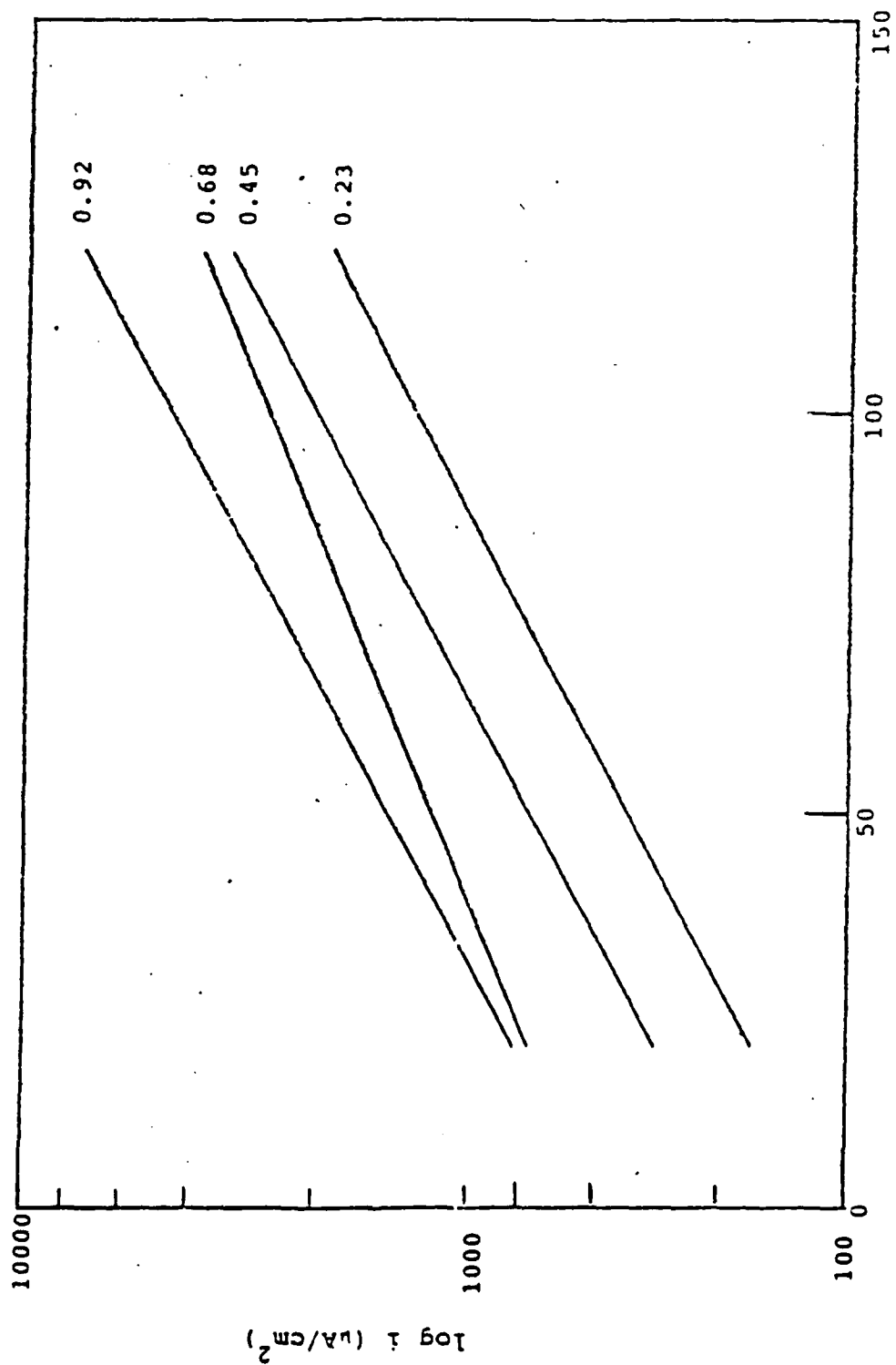


Figure 14. Galvanostatic polarization of calcium in  $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$  electrolytes at room temperature

the Li salt electrolyte, indicating that a faster rate is obtainable with the latter (aside from the fact that the conductivity of the Li salt electrolyte is higher than that of the Ca salt electrolyte). Secondly, there is a strong indication that the steady-state anodic dissolution of Ca in the Ca salt electrolyte depends on the concentration of  $\text{AlCl}_4^-$  and thus the reaction mechanism is controlled by Equation (2) rather than being a pure charge transfer reaction. The last distinct difference is the current density,  $i_c$ , at open circuit ( $\eta = 0$ ). It is observed, from comparison of Figures 13 and 14, that  $i_c$ , which might be referred to as the corrosion current density if  $i_c > i_0$  (the exchange current density), for the calcium salt electrolyte is at least one order of magnitude higher than that for the Li salt electrolyte. This difference might stem from the fact that the mechanisms of anodic dissolution in these two electrolytes are quite different. More elaborate experimentation is required to further elucidate the marked difference in kinetics and mechanism for the dissolution of Ca metal in  $\text{LiAlCl}_4$  and  $\text{Ca}(\text{AlCl}_4)_2$  electrolytes.



#### SECTION IV

##### CATHODE DEVELOPMENT

Cathode development was determined following discharge in hermetically sealed glass test cells. Each glass cell would hold one cathode measuring 0.54 X 0.687 inches, two anodes, separator, and up to 20 cm<sup>3</sup> of electrolyte. Each cell was constructed cathode limited in order to observe the total life and capacity of the cathode, with no capacity reductions caused by a shortage of anode or electrolyte materials.

Cathode material contained Shawinigan carbon black blended with a Teflon binder. The cathode material was dry pressed to an expanded nickel grid using a fabrication pressure of 15 LB/in<sup>2</sup> on the cathode surface. Cathode thickness varied with the amount of cathode mix used. The pressed cathodes were then dried at +100°C for 24 hours.

Cells were discharged in order to determine an optimum cathode current density and thickness for a given fabrication density. Initial tests used cathodes containing 95% carbon black and 5% Teflon. Each cathode contained 0.10 gms of cathode mix. An excess of 1.5M LiAlCl<sub>4</sub> electrolyte was used in all tests. The cells were discharged at +20°C using constant resistive loads of 60, 200, and 390 ohms. Figures 15, 16, and 17 show the resulting discharge curves. The cells discharged under a 60 ohm load produced an average matrix utilization of 0.22 AH/cm<sup>3</sup>. The cells discharged under a 200 ohm load produced a current density of 2.7 mA/cm<sup>2</sup> and produced an average matrix utilization of 0.35 AH/cm<sup>3</sup>. The cells discharged under a 390 ohm load produced a current density of 1.4 mA/cm<sup>2</sup> and produced an average matrix utilization of .50 AH/cm<sup>3</sup>. As the resistive load increased, the current density

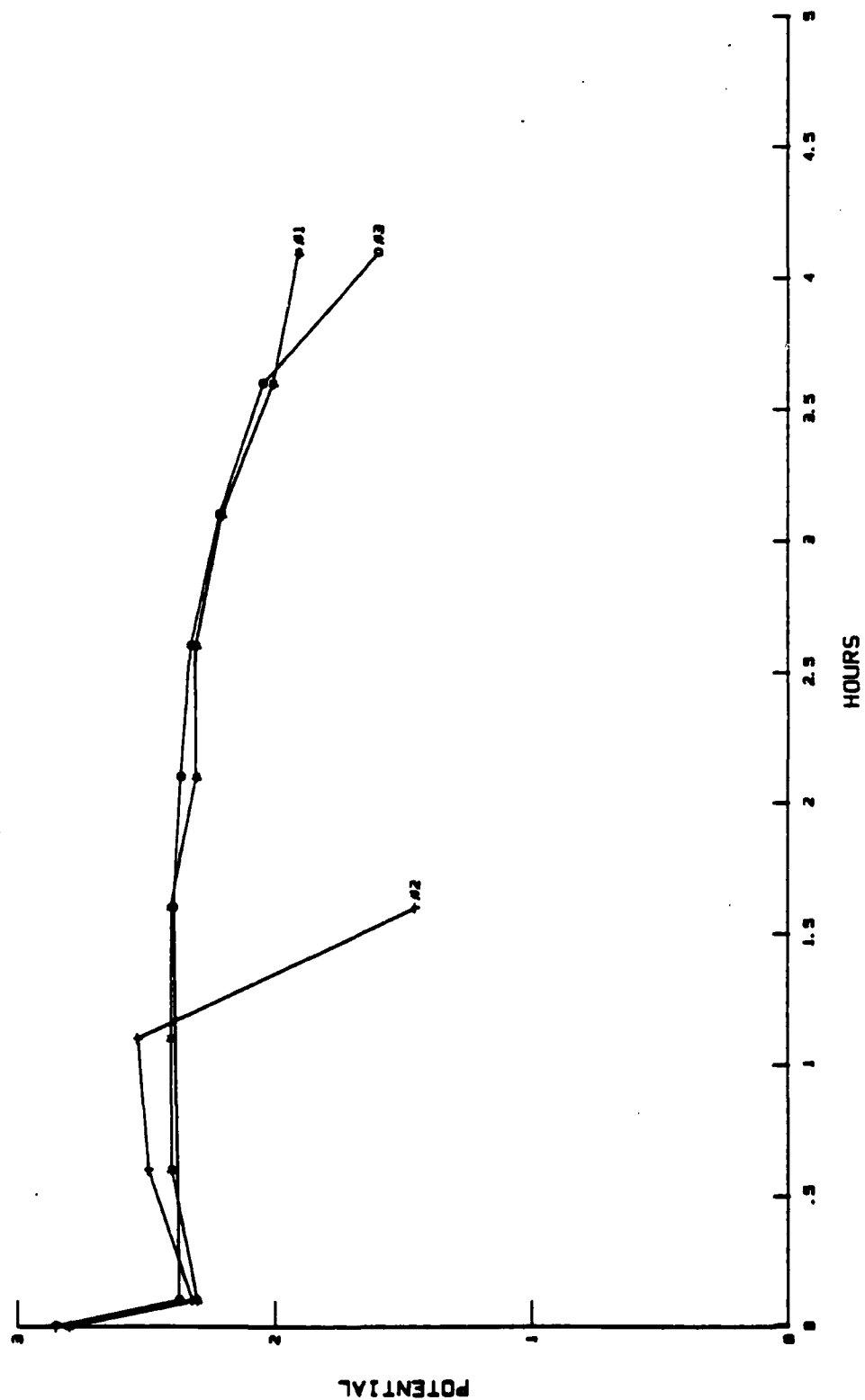


Figure 15. Pressed-5% TFE-0.05gm/side-60 ohm

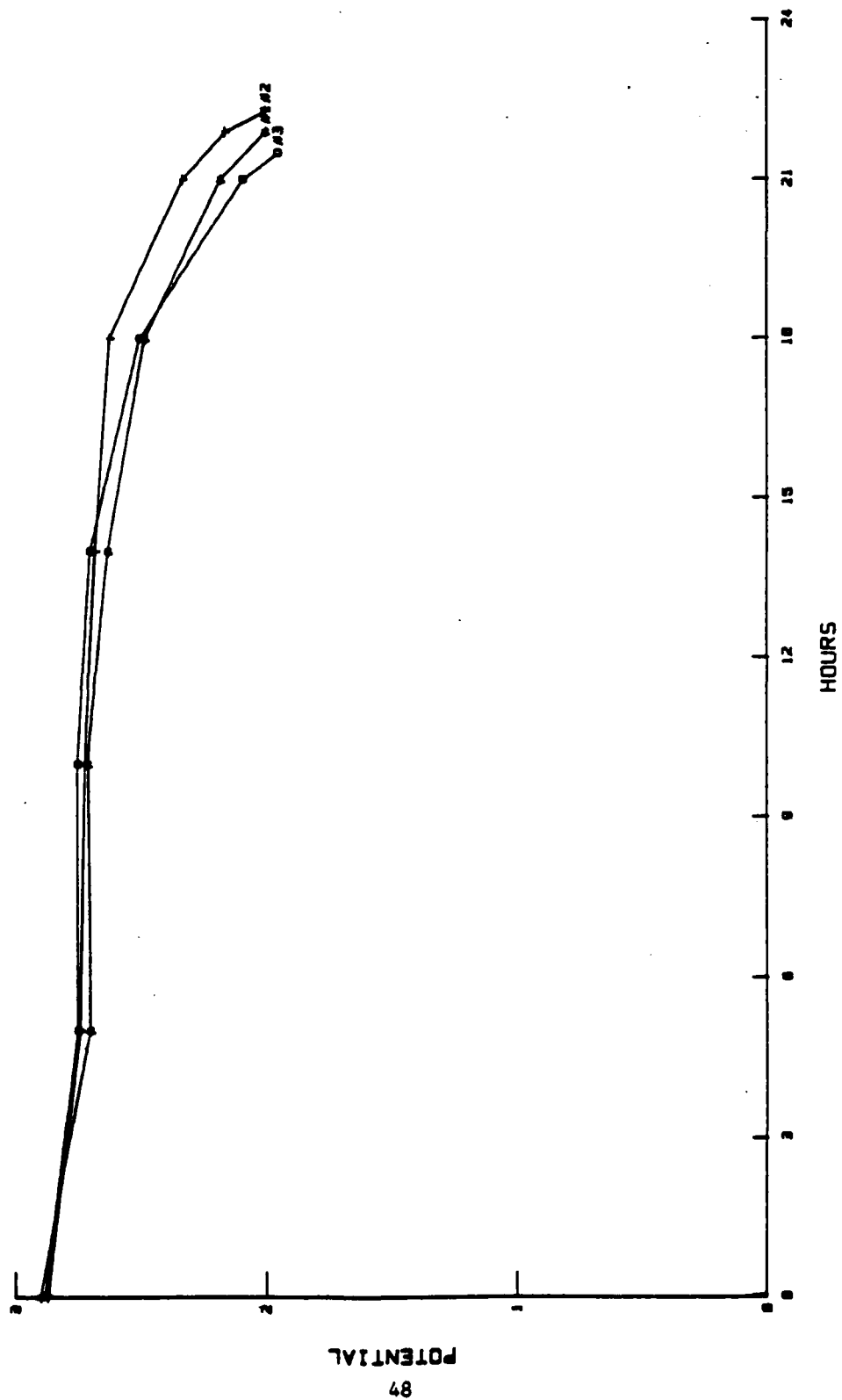


Figure 16. Pressed--5% TFE--0.5 $\mu$ m/side--200 ohm

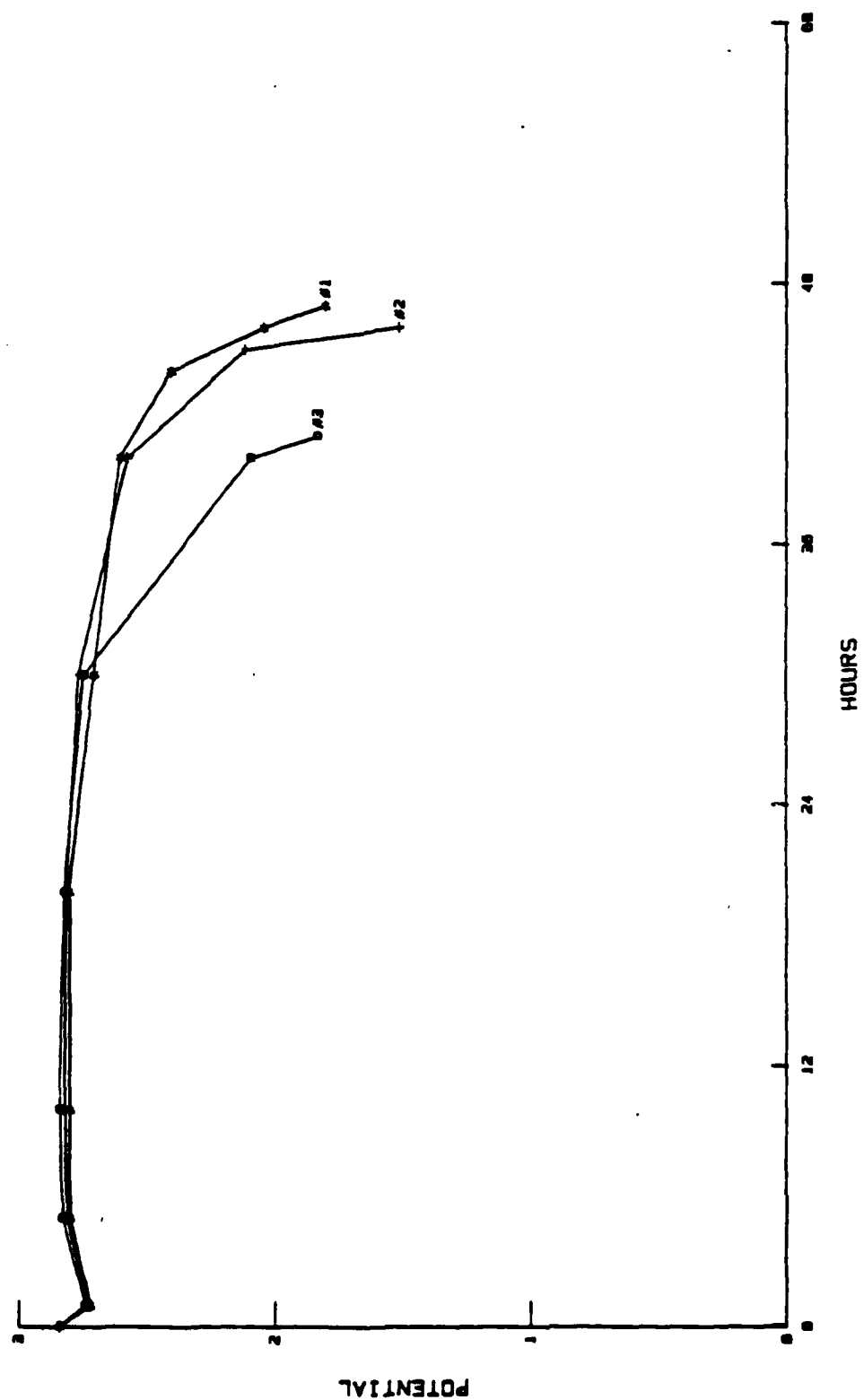


Figure 17. Pressed--5% TFE--0.05gm/side--300 ohm

decreased and the matrix utilization improved. A performance summary of Figures 15, 16, and 17 are summarized in Table 10.

Additional cathode testing used cathodes containing 0.20 gms of material instead of 0.10 gms. The cells were discharged under constant resistive loads of 200 and 390 ohms. Figures 18 and 19 show the resulting discharge curves. The cells discharged under 200 ohms produced an average matrix utilization of  $0.39 \text{ AH/cm}^3$ . This matrix utilization was a slight improvement over the 0.10 gm cathode discharged under a 200 ohm load. The 0.20 gm cathode discharged under a 390 ohm load produced a matrix utilization of  $0.46 \text{ AH/cm}^3$ . This was a drop from the matrix utilization resulting from the cathodes weighing 0.10 gm and discharged under a 390 ohm load. A performance summary of Figures 18 and 19 are summarized in Table 10.

All tests previously described contained 5% Teflon binder. Another group of cells were fabricated containing 3% and 10% Teflon binder. Each cathode contained 0.10 gms of cathode mix. The cells were discharged under a 390 ohm load at  $+20^\circ\text{C}$ . Figures 20 and 21 show the resulting discharge curves. Cell performance is summarized in Table 10. Table 10 shows that the cathodes containing 3% Teflon produced the highest matrix utilization,  $0.56 \text{ AH/cm}^3$ , and a very high specific capacity, 3.14 AH/GM. However, the 3% Teflon cathodes had poor mechanical properties thus making handling difficult. While electrical performance of such cathodes was satisfactory, they were too delicate to be used in full size cell production.

TABLE 10  
CATHODE PERFORMANCE

<u>Figure No.</u>	<u>Cathode</u>	<u>Load</u>	<u>Temp</u> <u>°C</u>	<u>AH. to 2.0V</u>	<u>Ave.Pot</u>	<u>AH/cm<sup>3</sup></u>	<u>AH/GM</u>
15	95% C.Black,5% TFE,0.10 gms	60	+20	0.167	2.320	0.22	1.37
16	95% C.Black,5% TFE,0.10 gms	200	+20	0.217	2.620	0.35	2.17
17	95% C.Black,5% TFE,0.10 gms	390	+20	0.308	2.720	0.50	3.08
18	95% C.Black,5% TFE, 0.20 gms	200	+20	0.331	2.605	0.39	1.66
19	95% C.Black,5% TFE, 0.20 gms	390	+20	0.386	2.762	0.46	1.93
21	90% C.Black,10% TFE, 0.10 gms	390	+20	0.346	2.521	0.46	3.46
20	97% C.Black, 3% TFE, 0.10 gms	390	+20	0.314	2.551	0.56	3.14
	97% C.Black, 3% TFE, 0.10 gms	390	+20	0.259	2.437	0.40	2.59
	(sintered)						

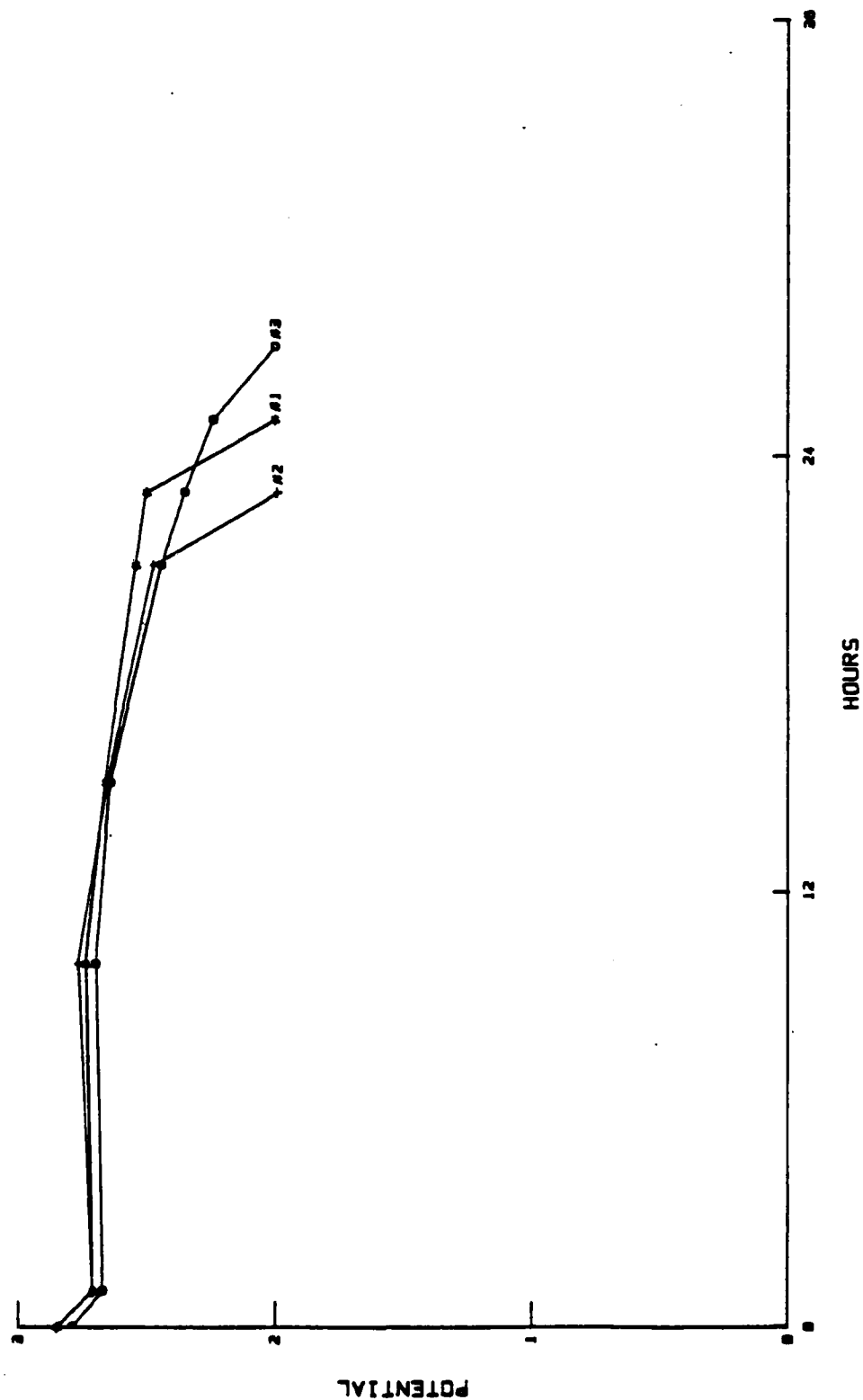


Figure 18. Pressed--5% TFE--0.1 gm/side--200 ohm

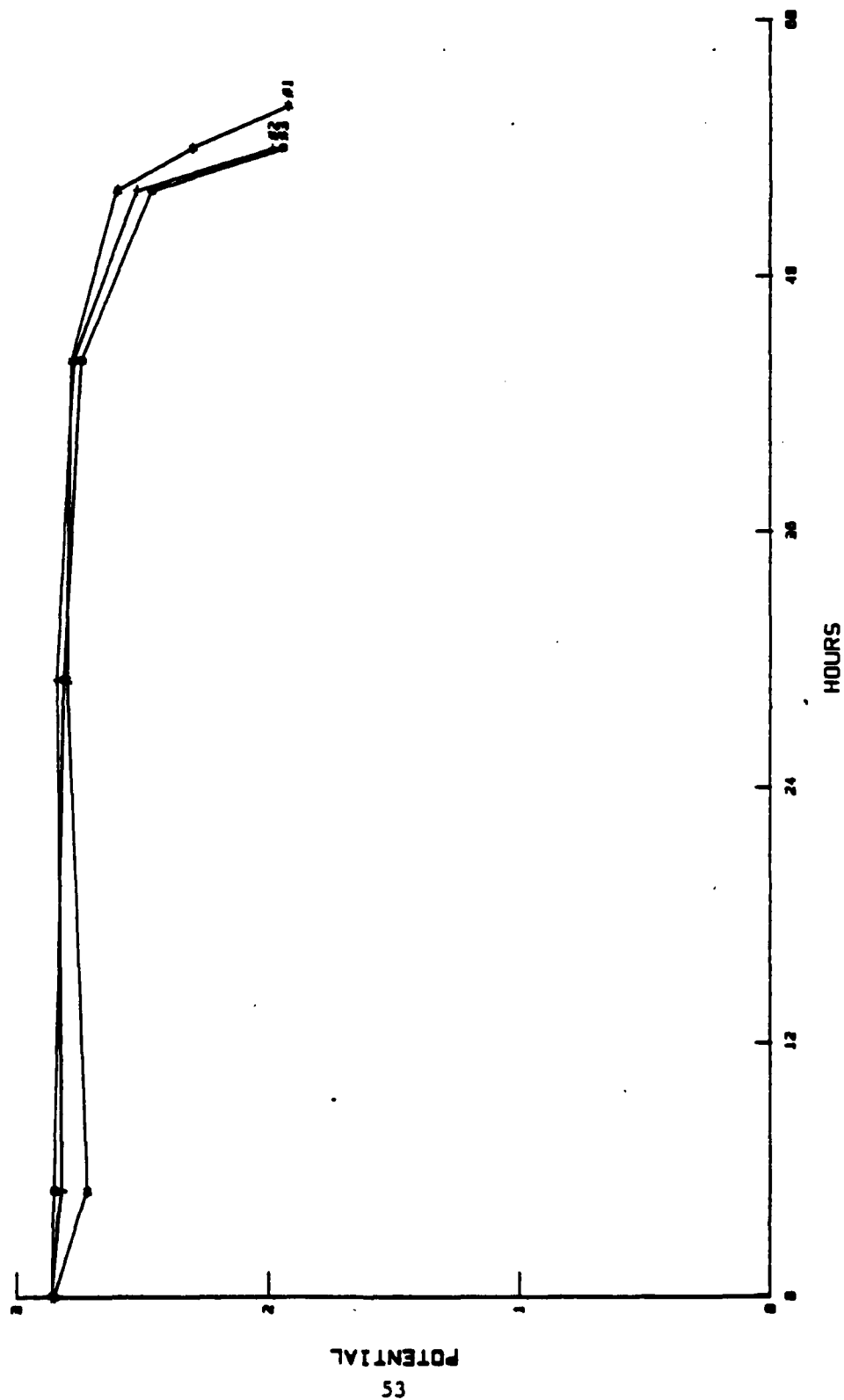


Figure 19. Pressed--5%TFE--0.1 gm/side--390 ohm



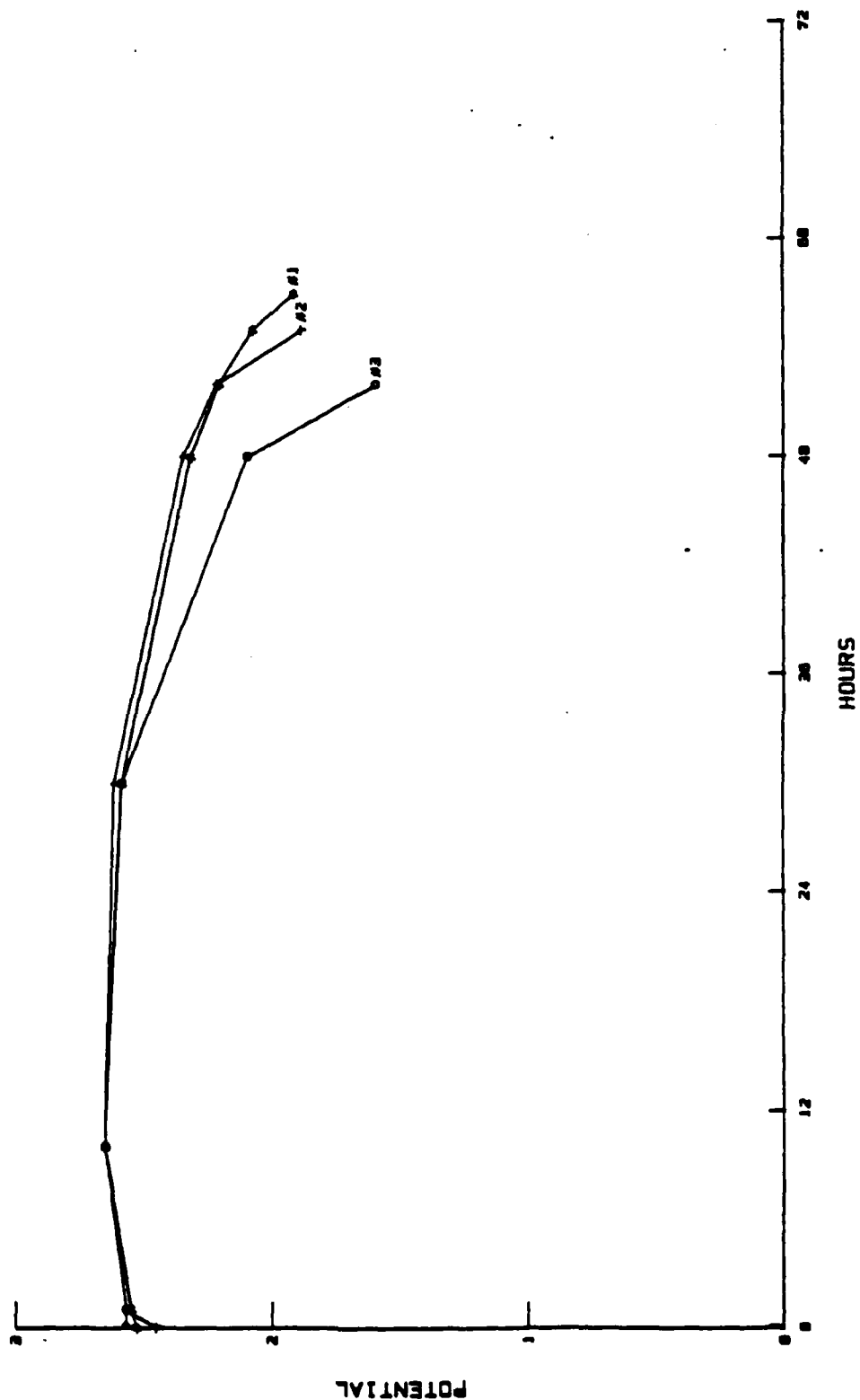


Figure 20. 3% TFE--0.05 gm/side--390 ohm

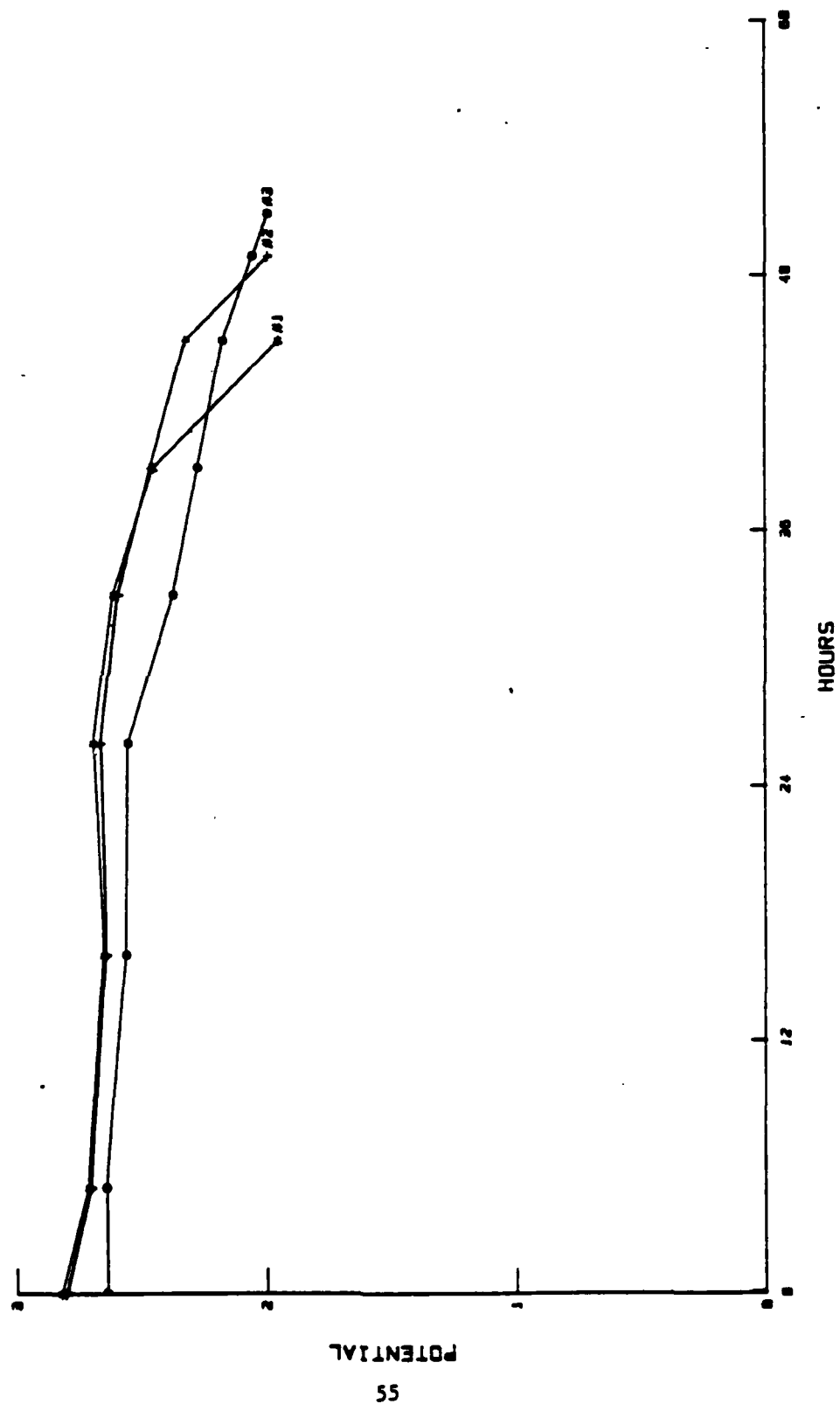


Figure 21. 10% TFE--0.05 gm/side--390 ohm

In order to improve the mechanical properties of 3% Teflon cathodes, the cathodes were sintered at +600°F for 15 minutes. The baking process caused the Teflon binder to flow and mix more uniformly throughout the cathode thus resulting in a more strongly bound cathode. The performance of sintered 3% cathodes is summarized in Table 10. Table 10 shows overall electrical performance of these sintered cathodes was inferior to the 3% cathodes tested earlier. Mechanical properties, however, were improved following the sintering process.

Table 11 shows the maximum number of cathodes which could be built into a 14 AH cell having a maximum volume of 3.2 in<sup>3</sup> and a cathode capable of providing 0.50 AH/cm<sup>3</sup>. A cathode made from 0.10 gms of mix containing 95% carbon black and 5% Teflon has a matrix utilization of 0.50 AH/cm<sup>3</sup> when discharged at 1.4 mA/cm<sup>2</sup>. Table 11 shows that a matrix utilization of 0.50 AH/cm<sup>3</sup> and current density of 1.4 mA/cm<sup>2</sup> requires that no less than ten cathodes be built into the cell.

Table 11. Cell Design Printout

Utilization = 0.5  
 Excess Calcium = 0.10  
 Separator Thickness = 0.005

<u>Cathode Number</u>	<u>Cathode Thickness</u>	<u>Current Density</u>	<u>Anode Thickness</u>	<u>Total Separator</u>	<u>Total Thickness</u>
1	0.7397	13.4228	0.0991	0.0100	0.9480
2	0.3698	6.7114	0.0661	0.0200	0.9580
3	0.2466	4.4743	0.0496	0.0300	0.9680
4	0.1849	3.3557	0.0397	0.0400	0.9780
5	0.1479	2.6846	0.0330	0.0500	0.9880
6	0.1233	2.2371	0.0283	0.0600	0.9980
7	0.1057	1.9175	0.0248	0.0700	1.0080
8	0.0925	1.6779	0.0220	0.0800	1.0180
9	0.0822	1.4914	0.0198	0.0900	1.0280
10	0.0740	1.3423	0.0180	0.1000	1.0380
11	0.0672	1.2203	0.0165	0.1100	1.0480
12	CELL WIDTH EXCEEDS LIMITS				

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